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Proceedings of the Society

WEST RIDING AND SCOTTISH SECTIONS

Meetings held at the Great Northern Victoria Hotel, Bradford, on 9th March 1950, Mr. J. M. GOODALL in the chair; and at the St. Enoch Hotel, Glasgow, on 14th March 1950, Mr. E. D. KENNEDY in the chair

The Cuticle of Wool

N. GRALÉN

Friction between wool fibres is smaller than friction between other fibres. This is explained by a thin fibre coating, the epicuticle, which was discovered by means of the electron microscope. The epicuticle is resistant to chlorine, acids, and enzymes. Alkaline treatment perforates it. The cuticle below the epicuticle consists of an intermediate layer, the exocuticle, and the scale substance proper, the endocuticle. The epicuticle prevents diffusion of large molecules, e.g. those of dyes. The Allwörden reaction and staining tests for damage are explained by the existence of the epicuticle. It is easily damaged by mechanical treatments. Its removal gives an increase in fibre friction and thereby anti-felting properties. The importance of the frictional properties of fibres for spinning and wearing qualities is stressed.

The textile properties of fibres are to a very large extent connected with their surface structure. When measuring the strength, extensibility, and elasticity of fibres we are mostly concerned with the core of the fibre, which forms the main part of it. Much research has been devoted to this part of the fibre, and its aim has been to explain mechanical properties on the basis of molecular structure, which is an essential task. But as soon as we convert the fibres to yarns or fabrics, we are very much concerned with their surfaces. In spinning, the fibres slip on each other, and their frictional properties are the basis of their spinning properties. In fabrics, strength and other mechanical properties are obtained by a combination of the mechanical properties of the fibres themselves and the frictional and adhesive forces between them. Our knowledge of the surface properties of fibres is much smaller than of the chemical and physical properties of their interior.

It is believed that most textile fibres have a cuticle, which is different from the rest of the fibre. The primary wall of cotton is physically different from the main part (the secondary wall) of the fibre, and probably also chemically[1]. Artificial fibres, e.g. viscose rayon, often have a skin, due to the method of extrusion and coagulation. In this example, the difference is mainly physical[2]. That is also probably true for other "skinned" macromolecular materials in nature, e.g. starch, the granules of which are supposed to be covered by a thin coating, which bursts during the swelling and gelatinisation of starch.

For wool, however, we are sure that a cuticle exists, which is both chemically and physically different from the rest of the fibre. The surface of wool shows a scaly appearance, which can be easily observed in the microscope. The cuticle forms a fairly large part of the fibre—various authors mention figures between 2 and 10%. This cuticle has been the subject of many investigations in various quarters[3–9], and during the last few years, since the establishment of the Swedish Institute for Textile Research in 1946, a Swedish group of research workers have entered the field.

These studies were begun with friction measurements on fibres. Such measurements had already been made[10–14], but we thought it essential to study the friction between single fibres, and therefore we constructed two pieces of apparatus for these measurements, the point friction meter and the twist friction meter, which have been described earlier[15,16]. From these measurements we were able to draw conclusions regarding the action of various anti-felting agents on wool (see p. 468). Some measurements of the friction between various fibres were made in the twist friction meter, where the contact between the two fibres is formed along an approximately straight line in the fibre direction. Table I gives a summary of these results. It shows that both nylon and natural silk, which are considered to be very smooth fibres, have frictional coefficients which are considerably higher than those of wool. In the dry state, the difference between the with-scale and anti-scale friction of wool is only about 0·05. In the wet state the

TABLE I
Static Coefficients of Friction of Fibres
(Average values)

Wool—	
With-scale	0·11
Anti-scale	0·14
Wool in water—	
With-scale	0·15
Anti-scale	0·32
Cotton	0·22
Jute	0·46
Silk	0·52
Viscose rayon	0·43
Acetate rayon	0·56
Casein	0·46
Nylon	0·47
Saran	0·55
Terylene	0·58
Steel	0·29

frictional coefficients increase, especially the anti-scale friction. The low friction of animal fibres is not surprising, perhaps, when the smooth feel of fur is considered. The smoothness of the wool surface is probably hidden by the crimp in the loose fibres and by the interlacing of fibres in the woven or knitted cloth.

The friction in the dry state of wool fibres is of the same order of magnitude as that of well lubricated metallic surfaces, and this low friction gives the impression of a very hard and smooth surface.

During an investigation of the wool fibre in the electron microscope we found what we think is the explanation of the low coefficient of friction[17]. After dissolving wool in a 1% sodium sulphide solution, a faint opalescence was left in the solution, and this opalescence did not disappear, even after a fairly long time. It was centrifuged down, washed, and investigated in the electron microscope. It proved to consist of very thin membranes, mostly folded, of fairly uniform thickness (Fig. 1). Later it was found that the same membranes were obtained from chlorinated wool simply by shaking the wool with water (Fig. 2). This way of preparing the membrane proves that it is located at the actual surface of the wool fibre. After treatment with chlorine and shaking with water the wool still has its fibre character, and even its scaly appearance under the microscope. In electron microscope replicas, the chlorinated fibre shows a striated structure in the fibre direction. These striations are not found, or at least are much less obvious, on the untreated native fibre.

The thickness of the membrane has been measured by means of the ordinary shadow-casting technique for the electron microscope, and was found to be 50–250 A. From these figures it is obvious that the membrane is only about 0·1% of the whole fibre. Therefore it is not the cuticle itself, but it certainly belongs to and forms part of the cuticle. As it is the outer part of the cuticle and forms a cover around the fibre, we have proposed the name *epicuticle* for it, in accordance with what is common for other biological tissues, e.g. the scales of insects.

The epicuticle is very resistant to chemical treatments. The methods of isolation show that it is resistant to chlorine and sodium sulphide. We also know that it is resistant to strong acids and to enzymes. In later experiments it has been found that a prolonged treatment with alkali or sodium sulphide results in perforation of the membrane, obviously the beginning of its destruction (Fig. 3). This might indicate that the epicuticle is not homogeneous but is affected only partly by alkali. In any case, its resistance is much greater than that of ordinary wool keratin, and this has led to the conclusion that it is not an ordinary protein. So far we do not know its exact composition. Fig. 4 shows an X-ray diagram of an isolated preparation. It is difficult to obtain it quite pure, because parts of the keratin always stick to it. No sign of an α-diagram was found, but indications of a β-diagram of keratin are superimposed in the diagram. There are, however, some other reflections, which do not belong to the ordinary keratin diagram.

A chemical analysis of the material is being undertaken. Various suggestions regarding the chemical nature of the epicuticle have been made, but none of them has been proved true. The chemical resistance might indicate a carbohydrate- or chitin-like structure. Also the possibility of a condensation product of waxes, originating from the same glands as the wool wax, has been mentioned. It certainly has not a cellular structure.

The epicuticle is one of the constituents of the wool cuticle. The rest of the cuticle has a rather complicated structure[18]. Several studies, with both the optical and the electron microscope, have been undertaken recently[6,8,19–25]. German workers have isolated a rather thick membrane (about 5% of the wool), which was supposed to be located between the cuticle and the cortex, and has therefore been called the *subcutis* or *Zwischenmembran*[3,5,23–25]. It is obtained by treatment of the wool with formaldehyde at 130°C. for several hours or with formamide or phenol at 130°C., followed by pancreatic digestion. In this way the cortex is dissolved or digested, and a tube is left, the assumed subcutis. We have shown that the tube has scale edges like the cuticle, and that a thin membrane quite similar to the epicuticle can be isolated from it by chlorine treatment, although the epicuticle in this case is partly thickened by hardened protein remnants (Fig. 5 and 6). Sometimes these remnants are very regularly arranged, e.g. as ridges along and parallel to the scale edges, and also but not so prominently in the fibre direction. The epicuticle also shows folds running in the fibre direction. In other places the remnants are more irregular lumps. These protein residues are supposed to belong to an intermediate layer between the epicuticle and the scales proper. We call this intermediate layer the *exocuticle*, and the scales themselves the *endocuticle*. The exocuticle (without hardening by phenol) can be digested by trypsin, which leaves the scales as a vesiculated substance (Fig. 7)[cf. 6, 20]. It is known that the scales adhere very strongly to each other, and in attempts to dissect the cuticle into scales by a micromanipulator it is difficult to isolate single scales; they stick together in bundles. This fact, together with the fact that the cuticle or part of it can be isolated as a tube (the subcutis of Zahn *et al.*), has even led to the view that the scales might

not be single cells, but the cuticle may have the shape of a folded sheath[26].

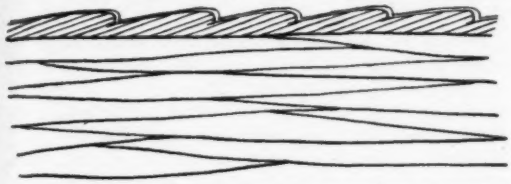

FIG. 8— Diagrammatic Representation of Cuticle with Underlying Cortical Cells. The hatched portion is the endocuticle

Our view of the cuticle is therefore represented diagrammatically by Fig. 8. The endocuticle (the scales) forms the main part of the cuticle. The outer part is the epicuticle, which is attached to the endocuticle by means of a protein layer, the exocuticle. This attachment is found primarily at the scale edges and also along other lines. The exocuticle seems to fill the thin space between endo- and epicuticle, but it is harder and more resistant along special lines or ridges running both across and along the fibres. The most prominent of these ridges run across the fibre, and there is probably also a thicker portion of the endocuticle at these ridges, which coincide with the scale edges. This is possibly not the final view, but it fits our present experimental results best.

The existence of an epicuticle or a similar membrane was predicted before our findings, from diffusion phenomena occurring in dyeing and staining[27]. If the epicuticle formed a continuous sheath around the whole fibre, probably no dye would penetrate the fibre. But this very thin membrane is easily damaged mechanically, e.g. when the sheep rubs against bushes, trees, or rocks, or when the wool is carded, combed, or woven. During the period on the sheep also a photochemical effect might be responsible for part of the damage. Tippy dyeing, a well known trouble, might be at least partly an effect of the mechanical

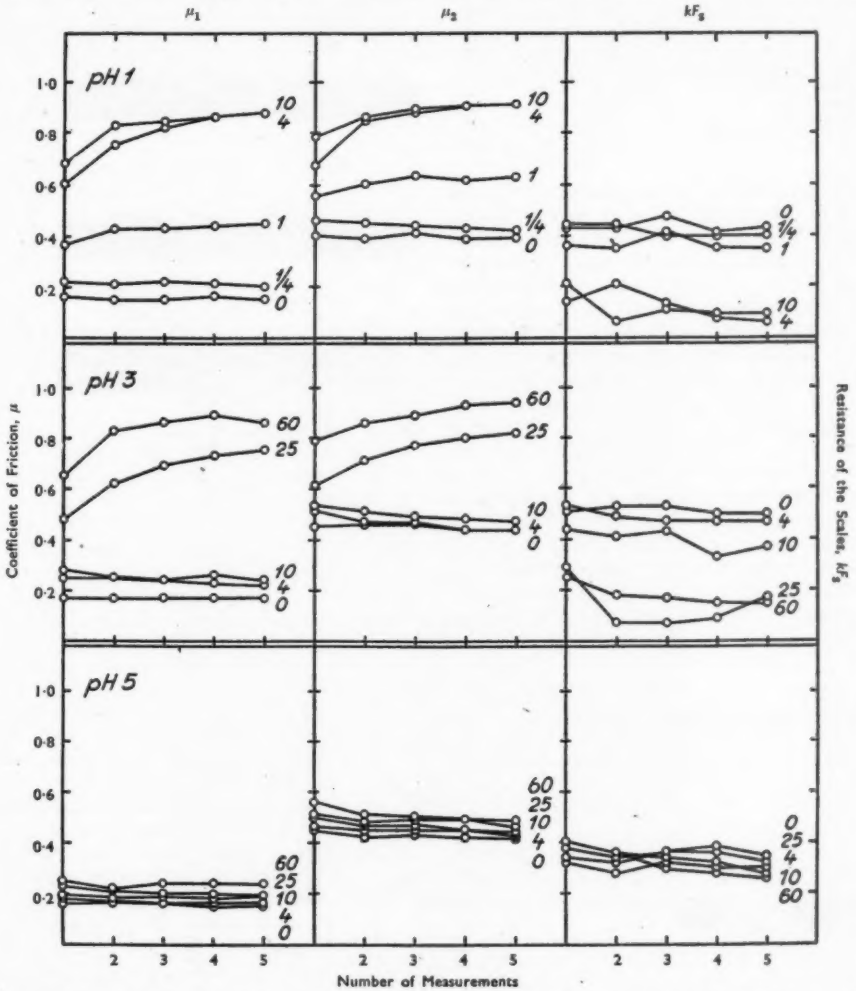

FIG. 10— Coefficients of Friction (μ_1 and μ_2) and Scale Resistance (kF_s) of Chlorinated Wool Fibres on Subsequent Measurement in the Twist Friction Meter. The chlorination was made with sodium hypochlorite (concentration 0·01% Cl). The figures in the diagram area give the times of treatment in minutes. From the top, the diagrams represent pH 1, pH 3, and pH 5.

or photochemical damage of the epicuticle of the wool when still on the sheep.

Lindberg[28] has confirmed that damage to the epicuticle produced by treatment with alcoholic potassium hydroxide gives more rapid and even dyeing (Fig. 9). Removal of the epicuticle without any other damage to the wool would certainly give a fibre that could be dyed with much less trouble than wool is dyed at present.

The frictional properties of wool and hence its felting properties depend very much on the cuticle[29]. The epicuticle is hard and smooth, and most anti-felting treatments (chlorination, alcoholic potash, permanganate, etc.) loosen the epicuticle and expose the underlying cuticular sheaths to abrasion during milling and laundering. This kind of treatment always gives an increase in friction (Table II).

TABLE II

Coefficients of Friction (in Water) of Wool Fibres after Various Anti-felting Treatments

Treatment	Coefficients of Friction		
	μ_2	μ_1	$\mu_2-\mu_1$
Untreated	0·38	0·21	0·17
Melamine	0·29	0·16	0·13
Benzoquinone	0·35	0·21	0·14
Dispersed silica	0·48	0·30	0·18
Alcoholic caustic potash	0·66	0·48	0·18
Alcoholic caustic soda	0·67	0·51	0·16
Hypochlorite (pH 1·5)	0·92	0·91	0·01
Chlorine in carbon tetrachloride ...	0·84	0·85	−0·01

The alcoholic potash does not remove the difference in friction, but as both the anti-scale and with-scale coefficients of friction are increased, fibre movement during laundering is diminished, and therefore the risk of felting is less. A severe mechanical treatment of the fabric will, however, cause felting, as the differential friction still exists. Chlorination in aqueous media affects deeper layers of the cuticle. Immediately after chlorination the difference in friction still exists, but only a few rubbings of the fibres against each other (i.e. subsequent measurements) rub off the scales or scale edges and eliminate the difference; simultaneously, there is a general increase in the friction, as the rubbing exposes the underlying rough surfaces of the fibres (Fig, 10). Treatment with plastics, e.g. melamine resin, does not change the frictional properties, and their anti-felting effect is probably due to "spot-welding" causing a decreased mobility of the fibres[30].

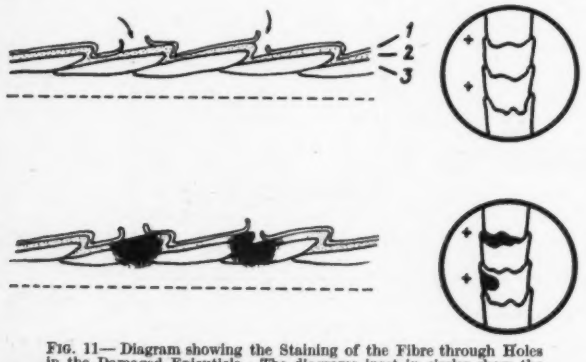

FIG. 11— Diagram showing the Staining of the Fibre through Holes in the Damaged Epicuticle. The diagrams inset in circles show the appearance of the fibre in the optical microscope[18].

Removal of the epicuticle would be very useful also for anti-felting, if done without any further damage, or possibly a slight softening of the nearest portion of the cuticle.

Several of the microscopical tests for damage to wool certainly depend on the existence and removal of the epicuticle. This is true of several staining tests, such as the Pauly test and the Methylene Blue test proposed by Whewell and Woods[27]. When the epicuticle is damaged, the dye penetrates through the holes and stains the keratin of the fibre (Fig. 11). The epicuticle is not stained, as far as we know.

The well known Allwörden test with chlorine water, which causes blisters on the intact fibres within a few minutes, is of special interest. Such blisters do not appear on alkali-treated or otherwise damaged wool. In this test the epicuticle acts as a semi-permeable membrane[31]. The chlorine readily diffuses through the epicuticle and reacts with the underlying exocuticle (Fig. 12). Soluble macromolecular products are formed, and exert an osmotic

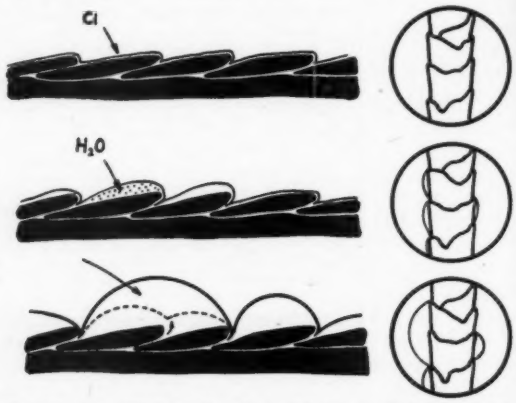

FIG. 12— The Allwörden Reaction. Chlorine penetrates the intact epicuticle, attacking the underlying layers. Osmotic swelling leads to the formation of blisters. The diagrams inset in circles show the appearance of the fibre in the optical microscope[18].

pressure on the membrane. The difference in refractive index between the inner and outer solutions makes the blisters visible even if the membrane itself is too thin to be observed. This test shows that the epicuticle sticks to the rest of the cuticle especially well along lines or ridges, which partly coincide with the scale edges, and partly run in other directions. It also shows that the epicuticle is fairly extensible, so that swelling and also some stretching of the fibres can occur without bursting the epicuticle.

The rôle of the frictional properties of the fibre in spinning wool and in the wearing properties of wool fabrics should also be noted[32]. It is known that chlorinated fibres give rise to a smaller number of ends down in spinning, due to the increase of friction between the fibres. Wearing properties might also be enhanced by a reduction of the fibre slippage.

In the electron-microscopic examination of the epicuticle we have come across

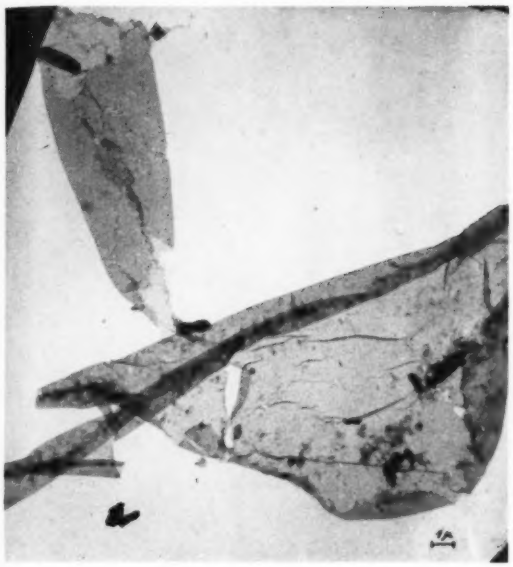

FIG. 1 — Epicuticle, isolated by Treatment with 1% Sodium Sulphide Solution (16 hr. at 60°C., 7 days at 30°C.)

FIG. 2 — Epicuticle, isolated by Mild Chlorination

FIG. 3 — Epicuticle, isolated by Sodium Sulphide Solution, shadow-cast

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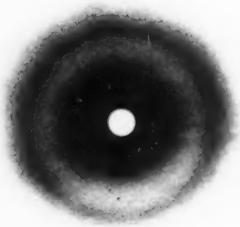

FIG. 4.—X-Ray Diagram of Epicuticle, obtained by Bromination of Wool. The sample contains about 75% foreign matter (keratin). The rings correspond to the atomic spacings 9·3, 4·5, and 4·1 A.

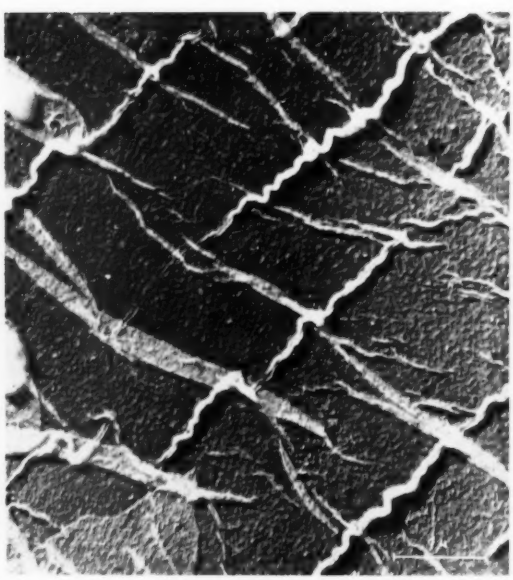

FIG. 5 and 6.—Cuticle Preparation, obtained by Treatment with 50% Phenol at 100°C. for 2 hr. followed by Digestion with Trypsin at pH 8·9. The background is the epicuticle. The scale edges (in Fig. 5) and the exocuticle ridges (in both Fig. 5 and 6) are obvious. Fig. 6 is shadow-cast and turned through 90° from Fig. 5

Fig. 7— Vesiculated Scale Substance, obtained after Tryptic Digestion

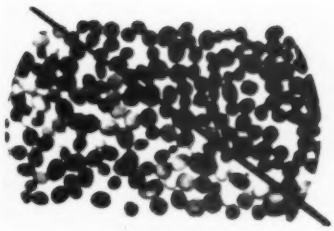

Fig. 9— Cross-sections of Wool Fibres dyed with the Same Dyebath Concentration of a Neolan (Ciba) Dye. The right-hand portion is treated with alcoholic caustic potash, the left-hand portion untreated. The treated fibres show uniform dye absorption, whereas the untreated fibres are dyed very unlevel, because the epicuticles of some of them are damaged, while those of others are not[28]

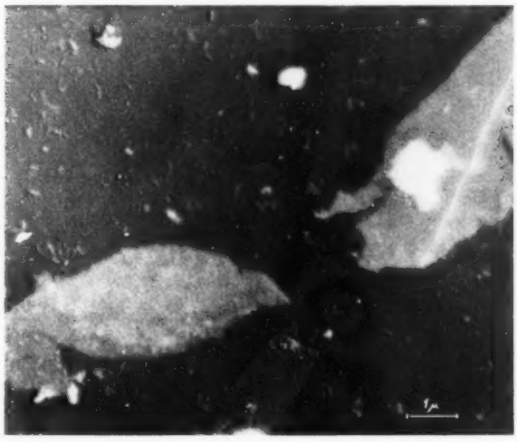

Fig. 13— Epicuticle obtained by Bromination

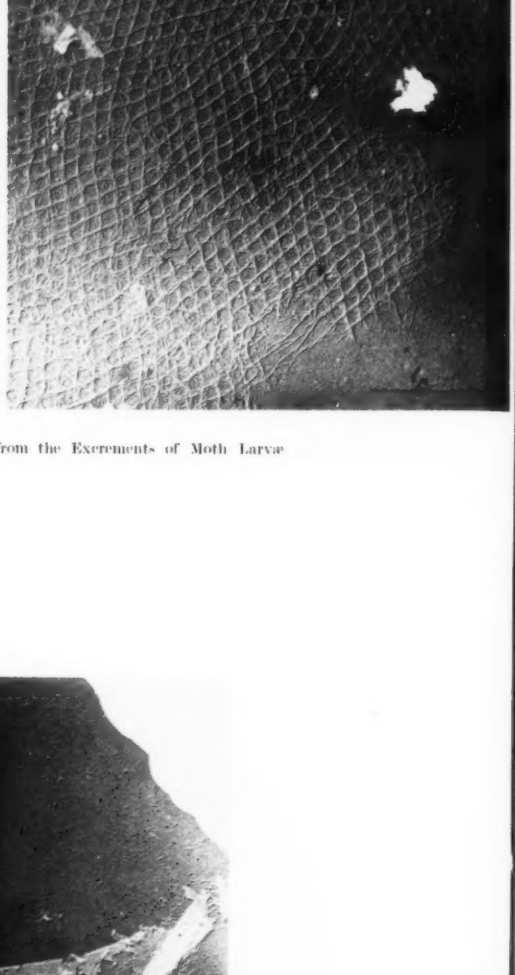

FIG. 14 and 15— Net Structure, obtained from the Excrements of Moth Larvæ

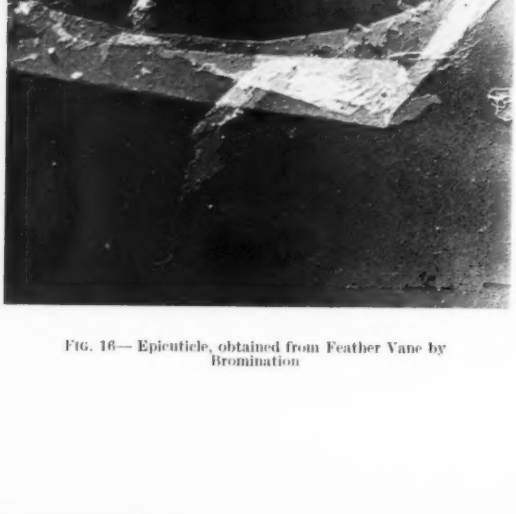

FIG. 16— Epicuticle, obtained from Feather Vane by Bromination

some phenomena, which have not yet been properly explained, but which might be of some interest. If the epicuticle is prepared by means of bromine water, it often shows small dots scattered over the membrane (Fig. 13). Sometimes the dots are concentrated along a line crossing the epicuticle. This phenomenon might be related to the lines of attachment mentioned earlier.

In our search for methods of isolating the epicuticle we also tried enzymatic breakdown of the cortex and cuticle keratin. As the clothes' moth larva has very effective keratin enzymes in its alimentary canal, we investigated the excrements of larvæ in the hope of finding some epicuticle there. The excrements were a very heterogeneous mixture of digested and undigested parts of the wool, cortical spindle cells, etc. Among this we found a very beautiful net structure, shown in Fig. 14 and 15. It has a very fine fibrillar structure, and looks like a fisherman's net, with the threads running primarily in three directions. At first we thought this to be a skeleton of the epicuticle, but that interpretation is rather incredible. How this fine network is formed we do not know. It might be parts of the intestinal wall[33]; it might also be formed by bacteria or enzymes from the intestine. The latter interpretation is supported by the observation of an increase of the material in the excrements after some time.

It should be mentioned here that the epicuticle is found also in other animal tissues besides wool. It is found on the hairs of other animals, on the shells of reptiles, and on the surface of the vanes of feathers (Fig. 16). In the last-mentioned case it forms a comparatively large part of the vanes, probably about 1%. It is thicker than on wool, but has the same smooth appearance. Its chemical resistance to treatment with phenol is less than that of the wool epicuticle.

The importance of the structure of the wool cuticle has been made clear by the examples mentioned from the textile application of our knowledge. But further research is necessary to obtain better information regarding the chemical and physical structure of the various parts of the cuticle.

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Discussion

WEST RIDING SECTION

Dr. P. ALEXANDER: Recent experiments of ours indicate that the cuticle of wool is composed of β-keratin and that the bulk of the wool inside consists of α-keratin. This is of great practical and theoretical interest, since the β-form has powerful interchain hydrogen bonding, resulting in a much stronger structure than the α-form, in which most of the hydrogen bonding is within the same chain. It would therefore appear that the wool has a tough outer shell with an elastic interior. This conclusion is supported by observations on the structure of the cuticle in stretched hair. When human hair is stretched to 60% extension, the surface breaks up and the scales come off, suggesting that the surface is not so elastic as the interior.

The evidence for the different structures of the cuticle and the cortex was obtained from wool which had been treated with peracetic acid, so as to oxidise all the available disulphide bonds without attacking any other major grouping in the wool. The wool, after this treatment, is freely soluble in ammonia, leaving a membrane as a residue which forms the major part of the cuticle. This insoluble membrane is in the β-form. If the ammonia solution, which contains more than 90% of the wool substance, is acidified, a protein is precipitated which is of a high molecular weight. Since this latter material gives the α X-ray diagram, it can be concluded that treatment with peracetic acid does not "denature" the wool protein, and that the membrane isolated is probably in the β-form in the original wool, as there seems no reason why 10%

of the wool should be "denatured" by the reagent when the remaining 90% is not.

Prof. GRALÉN: Dr. Alexander has kindly submitted to us a sample of the membrane, isolated by means of ammonia solution after peracetic treatment. Mr. Philip and Mr. Lagermalm investigated it in the electron microscope. It contains not only cuticular structures (epi-, exo-, and endocuticle), but also a large number of cortex cells. Zahn and Haselmann[25] have found recently that the outer layers of the cortex are chemically more resistant than the inner cells. Dr. Alexander's preparation might therefore be identical with the cuticle plus this resistant layer. In any case it is a mixture of cuticle and cortex elements. The high percentage of the wool contained in the preparation also supports this suggestion.

The X-ray diagram of the sample of epicuticle and exocuticle (Fig. 4) indicates that the protein remnants are in the β-form.

Dr. R. L. ELLIOTT: Unpublished work with the electron microscope at Bradford Technical College, privately communicated to Prof. Gralén, confirms his work, in so far as removal of the epicuticle by chlorination gives a much sharper edge to the scale structure. In addition, it has not been possible to repeat the peracetic acid–ammonia treatment of wool so as to leave 10% subcuticle as stated by Dr. Alexander, such treatment always leaving cortical cells and scales in addition to the alleged subcuticle.

Whilst the epicuticle may be waxy in nature, the photographs shown by Prof. Gralén of the epicuticle after sodium sulphide treatment suggest a composition containing at least two components, one of which may be waxy in nature as suggested, whilst the other may be a protein, of much simpler amino-acid composition than the main body of the fibre. For example, it may be lacking in sulphur-containing amino acids (hence the inability of moth larvæ to digest the epicuticle completely); and it may also be lacking in the "coupling-group" amino acids, such as tyrosine and tryptophan, explaining the failure to stain by the Pauly reagent. This would bring it into line with the silk fibre in some respects, for this is an "extrusion" material, as may be the epicuticle of the wool fibre, whilst the development of the main structure of the wool (cortical cells, scales) is from special cells in the hair-follicle.

It appears that there must be close co-operation between chemists and biologists on the properties of the follicle and of the various portions of the wool fibre before finality can be reached.

Prof. GRALÉN: Even if the scale edges look sharper after chlorination, the difference in friction between the two directions is reduced, because the chlorine softens the material under the epicuticle. The suggestions Dr. Elliott puts forward regarding the nature of the epicuticle are interesting.

Prof. J. B. SPEAKMAN: In view of the work of Professor Gralén and his colleagues, it is now recognised that Whewell and Woods' sensitive test for damage is based on the presence or absence of the epicuticle. Using this test, they found that damage was caused by such mild treatments as rolling fibres between finger and thumb, and was fairly severe after a soap-scoured wool had been carded. The usual methods of processing wool are thus likely to break up or crack the epicuticle to such an extent that it may not interfere seriously with the dyeing of yarn or pieces, though difficulty may arise with solvent-scoured wool.

I was greatly interested in the photograph of the "woven" structure in the excrement of the moth larvæ. Though not exactly the same, it reminded me of Professor Astbury's electron micrograph of the cuticle of an earthworm. Professor Gralén would find the micrograph interesting if it is not already known to him.

As regards Dr. Alexander's suggestion that the cuticle of wool may have the β-configuration, this seems unlikely in view of the fact that the X-ray photograph of unstretched wool does not show mixed β- and α-patterns. If the cuticular layers did amount to 10% of the substance of wool, as Dr. Alexander has suggested, a β-photograph should be detectable in the X-ray diagram of unstretched wool. It seems more likely that the β-configuration of the residue left after wool has been given the treatment described by Dr. Alexander is due to supercontraction.

Prof. GRALÉN: I agree that rather considerable damage is done to the wool in ordinary processing. However, rolling between finger and thumb might be an even more severe mechanical treatment of the epicuticle than carding after soap scouring. On the other hand, this damage to the epicuticle is not homogeneous. A homogeneous "damage" which would improve levelness might be more easily obtained by chemical instead of physical means, but before such a process can be developed, we must know more about the structure of the cuticle.

The micrographs of the cuticle of the earthworm show fibrils in two almost perpendicular directions, whereas the net structure from the moth larvæ excrement has three dominant fibril directions. The microfibrils from the moth larva seem to be thinner than those from the earthworm (50–100 against 200–300 A.).

Mr. J. SIKORSKI*: Prof. Speakman's statement is supported by the experimental evidence; X-ray photographs of the untreated wool keratin, even taken with very prolonged times of exposure, have never revealed the existence of reflections which would suggest the presence of extended polypeptide chains. Such reflections would be seen even if only a small percentage of the β-keratin were present in the normal wool fibres, as is actually proved by an X-ray photograph of a sample containing unstretched α-keratin and steam-set β-keratin wool fibres, in a ratio of 9 : 1 in the cross-section of the X-ray beam; both α- and β-reflections could be readily distinguished.

The two crystallographic forms of the powdered precipitate and residue, reported by Dr. Alexander, do not necessarily imply the existence of the β-form of keratin in the insoluble membrane. These results could be interpreted as due to the different effects of the dispersing and precipitating media on the chemically heterogeneous fractions of the wool fibre.

* Communicated

COMMUNICATIONS

The Influence of Substituents on (1) the Decomposition of Diazo Compounds in Acid and Alkaline Solution, and (2) the Alkaline Reduction of Aromatic Nitro Compounds

H. H. HODGSON, W. H. H. NORRIS, and E. R. WARD

Conductivity data indicate that diazonium ions in acid solution constitute the greater part of the diazonium–diazo equilibrium—

$$Ar{-}\overset{+}{N}{\equiv}N{:}\}\bar{X} \rightleftharpoons Ar{-}N{=}N{-}X$$

these are stabilised by kationoid and destabilised by anionoid substituents. In alkaline solution, the more complex system—

$$\underset{\text{(I)}}{\rangle C{-}\overset{+}{N}{\equiv}N{:}\}\bar{O}H} \rightleftharpoons \underset{\text{(II)}}{\rangle C{-}N{=}N{-}OH} \rightleftharpoons [\rangle C{-}N{=}N{-}O \longleftrightarrow \underset{\text{(III)}}{\rangle C{-}N{-}N{=}O}\,]^{-}Na^{+}$$

when disturbed (e.g. by evolution of nitrogen from (I), or by hydrolysis of (III), etc.), will then be further upset by the reactivity of (II) with the products from (I) and (III). Kationoid substituents will confer greater reactive power on the diazohydroxides (II) than anionoid substituents, so that the ultimate rate of decomposition of the alkaline system will be enhanced in the reverse direction to that in acid solution. This viewpoint explains Jolles' results[12] on the stability of alkaline diazoates, and his work on diazo resins is also briefly discussed.

(2) Unlike reduction of aromatic nitro compounds direct to amines in acid solution, the reduction in alkaline media is complicated by the *aldol condensation* of the second (nitroso) with the third (hydroxylamino) reduction product to form a relatively stable azoxy compound. Anionoid substituents will, therefore, tend to inhibit further reduction by making the azoxy compound, and subsequently the azo compound, more anionoid towards the anionoid reducing agent, while kationoid substituents will have the reverse effect. The anomalous case of the reduction of *p*-dinitrobenzene by sodium hydrosulphide[19] mainly to *pp'*-dinitroazobenzene is discussed, and found to depend on solvent action on the nitro group.

(1) INTRODUCTION

Diazo compounds are highly ionised in mineral acid solution, and their diazonium ions decompose with evolution of nitrogen according to the unimolecular law at any particular temperature, irrespective of whether their anion is chloride, bromide, sulphate, or nitrate[1]. From the main equation for the decomposition—

$$ArN_2^{+}\}X^{-} + H_2O \rightarrow ArOH + H^{+}\}X^{-} + N_2$$

it follows that the acid concentration increases during the progress of the reaction, which, however, is not affected by the free mineral acid present, except that Cain[2] found the rate to fall when much sulphuric acid was present, while Euler[3] could not get consistent results for measurement of the acid formed as a means of interpreting the process.

MODIFICATION OF BLUMBERGER'S EXPLANATION OF THE ABOVE ANOMALIES

Blumberger[4] showed that both the Euler[3] and Cain[2] results are to be expected, but while his conclusions are pointers in the right direction, the interpretation of the various reactions requires drastic modification in the light of recent electronic theory. His thesis was that the main attack on the diazo compounds by water was accompanied by side reactions in which no acid was produced, and which are depicted as—

$$ArN_2X \rightarrow ArX + N_2 \qquad \text{(i)}$$

$$ArN_2^{+} + HX \rightarrow ArX + N_2 + H^{+} \qquad \text{(ii)}$$

where X was Cl in his paper, and Euler's failure[3] is thus explained. Cain's result is ascribed to the probable presence of $[ArN_2SO_4]^{-}$ anions, which decompose more slowly than the kation ArN_2^{+}. In support of this explanation, Blumberger found that the yield of monochlorobenzene was increased by adding chlorides to weakly acid solutions of benzenediazonium chloride.

Moreover, both Hantzsch[1] and Cain[2] showed experimentally that concentration did not affect the rate of decomposition, and although Hantzsch supposed Schwalbe, who held the opposite view, to be in error, Snow[5] has since proved that the rate of decomposition is somewhat retarded in concentrated solution.

It is on the present authors' fundamental assumption that diazonium ions and not covalent diazo compounds decompose when nitrogen is evolved that Blumberger's arguments require modification, since in (i) he has employed a non-ionic mechanism—

$$Ar{-}N{=}N{-}Cl \rightarrow Ar^{\bullet} + N_2 + Cl^{\bullet} \rightarrow ArCl + N_2$$

which Hodgson[6] has shown to be invalid for diazo decompositions in aqueous solution. Consequently (ii) is the more probable reaction which takes place concurrently with that of anionoid water, and it affects the diazonium ion only in the tautomeric equilibrium—

$$Ar{-}\overset{+}{N}{\equiv}N{:}\}\bar{X} \rightleftharpoons Ar{-}N{=}N{-}X$$

the respective mechanisms[7] are—

$$\rangle\overset{\delta+}{C}{-}\overset{+}{N}{\equiv}N{:}\}\bar{X} \rightarrow \rangle C{-}Cl + \overset{+}{H}\}\bar{X} + N_2$$

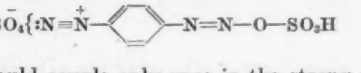
$$\delta^{-}Cl{-}\overset{\delta+}{H} \qquad \text{(No change in total acid)}$$

and

$$\rangle\overset{\delta+}{C}{-}\overset{+}{N}{\equiv}N{:}\}X \rightarrow \rangle C{-}OH + \overset{+}{H}\}\bar{X} + N_2$$

$$H{-}\overset{\delta-}{O}{-}\overset{\delta+}{H} \qquad \text{(Acid produced)}$$

It was established by Schoutissen[8] that tetrazotised *p*-phenylenediamine in concentrated sulphuric acid existed in the form—



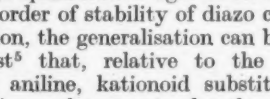
since it could couple only once in the strong acid, and a second coupling with β-naphthol could not take place until the mineral acid had been removed; thus the covalent diazo structure could be established for the second diazo group. This fact lends some support to Blumberger's view that $[ArN_2SO_4]^-$ anions exist, and the consequent shifting of the diazo–diazonium equilibrium in favour of the diazo form at very high concentrations would reduce the active concentration of the diazonium ion, with resultant falling off in the rate of decomposition.

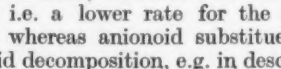
INFLUENCE OF SUBSTITUENTS ON STABILITY IN ACID SOLUTIONS

Although quantitative agreement is lacking for the exact order of stability of diazo compounds in acid solution, the generalisation can be made from Snow's list[5] that, relative to the stability of diazotised aniline, kationoid substituents confer stability, i.e. a lower rate for the evolution of nitrogen, whereas anionoid substituents promote more rapid decomposition, e.g. in descending order of stability of their diazotised forms—

p-Nitroaniline > Sulphanilic acid > α-Naphthylamine > β-Naphthylamine > Aniline > *o*-Toluidine > *p*-Xylidine.

This follows from the fact that kationoid substituents tend to withdraw electrons from the diazonium group and so prevent or retard the capture of an electron for its release as molecular nitrogen, while anionoid substituents tend to facilitate the latter process—

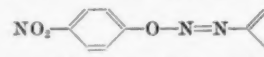




Addition of neutral metallic salts has been found in some cases to slow down decomposition; e.g. Schwalbe[1] found the rate for *p*-nitrobenzenediazonium chloride to be decreased by half, and Hantzsch and Thompson[1] by 40% when suitable additions of sodium chloride were made, a result which could be explained by a shift of the diazo–diazonium equilibrium in favour of the covalent non-decomposing tautomeride.

DECOMPOSITIONS IN NEUTRAL SOLUTION (CA. P_H 7)

The case of the decomposition of diazotised aniline[9] in the presence of calcium carbonate, sodium acetate, and, generally, in solutions buffered from pH 4·2 to pH 10·5, gives some idea of the complexity which now arises in the absence of mineral acid; here, mono-, bis-, and tris-azophenols are formed in varying proportions depending on the pH of the medium. Still greater complexity occurs when *p*-nitrobenzenediazonium sulphate[10] decomposes in the presence of calcium carbonate, when the reaction products identified were *pp'*-dinitrodiazoaminobenzene (approx. 40%) resulting from the hydrolysis of *p*-nitrobenzenenitrosoamine, 4-nitro-2-*p*-nitrobenzeneazophenol (approx. 10%) by solvolytic action of water on *p*-nitrobenzenediazonium hydroxide or salt and subsequent coupling of the *p*-nitrophenol formed with *p*-nitrobenzenediazohydroxide, a small mount of *pp'*-dinitrodiphenylamine by interaction of the nitrosoamine with the diazonium hydroxide above, and approx. 50% of an inseparable tar; another possible product is the diazo-oxide—



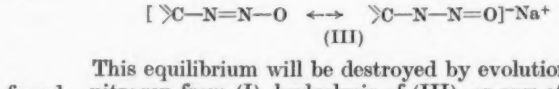
which would undoubtedly contribute to the tar yield. These results are in accord with the experience of Atkinson *et al.*[11], who found that the actual reduction of aryldiazonium salts in aqueous solution proceeded according to the general scheme—

$$RN_2X \rightarrow R{\cdot}R + R{\cdot}N{:}N{\cdot}R + R{\cdot}O{\cdot}R + R{\cdot}NH{\cdot}R + RX + R{\cdot}OH + R{\cdot}NH_2 + N_2$$

EFFECT OF SUBSTITUENTS IN ALKALINE SOLUTION

Jolles *et al.*[12] examined the decomposition of diazotised aniline, *o*-, *m*-, and *p*-toluidine, *o*- and *p*-anisidine, *o*- and *p*-phenetidine, and α-naphthylamine in alkaline solution, and concluded that the rules for the substituent effects were the reverse of those which apply to diazonium salts in acid solution, and that alkoxy groups in the *ortho* and *para* positions increase the rate of decomposition of the diazoates Jolles *et al.* offered no explanation of this reversal, so the following suggestions are made by the present authors—

In alkaline solution the following more extensive equilibrium system than in acid solution is set up—



This equilibrium will be destroyed by evolution of nitrogen from (I), hydrolysis of (III), or any other mode of decomposition, and these initiating disturbances will bring the diazohydroxide (II) into reaction with the reaction products from (I) and (III) (e.g. phenol, amine, etc.). For substituted diazohydroxides, kationoid substituents[13–15] will confer greater reactive power than anionoid substituents, and so the ultimate rates of decomposition will be in the reverse order to that in acid solution; i.e. an apparent reversal of effect.

THE DIAZO RESINS OF JOLLES

Jolles *et al.*[12] found that in alkaline solution many diazotised amines resinified on keeping, and, in the case of aniline, no less than 94·2% of resin was formed, for which the formula $C_{24}H_{18}ON_2$ was indicated by freezing-point measurements, while the formation of aniline on reduction with tin and hydrochloric acid suggested the resin to possess an azo structure. It will be seen that the above formula corresponds to—

$$C_6H_5{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}O{\cdot}N{:}N{\cdot}C_6H_5$$

or

$$C_6H_5{\cdot}C_6H_4{\cdot}C_6H_3(OH){\cdot}N{:}N{\cdot}C_6H_5$$

and that such types of compound could arise via Gomberg reactions[15] between diazonium hydroxides and phenol first formed in the initial decomposition, with coupling either at the phenolic oxygen or in the ordinary way. Since such reactions can take place at a variety of *ortho* and *para* positions, a complex mixture is inevitable, and hence the ultimate product will be a resin. The internal oxidation theory proposed by Jolles *et al.*[12] would be modified on this view by the circumstance that the oxidising agent will be benzenediazonium hydroxide. It would appear that the alkalinity of the decomposing mixtures is sufficient by formation of (III) to prevent substantial coupling of the phenol first formed. In such experiments, unless all traces of nitrous acid are removed before the solution of the diazotised amine is made alkaline, then it will contain some sodium nitrite, and nitrobenzene will result in yield depending on the amount of nitrite present[16]. This reaction proves the presence of benzenediazonium hydroxide in the equilibrium system.

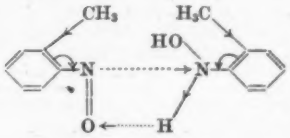
(2) INTRODUCTION

Whereas the reduction of nitrobenzene with zinc in mineral acid media gives aniline directly, in neutral aqueous suspension (generally containing sodium, ammonium, or calcium chloride in solution) it proceeds only as far as β-phenylhydroxylamine; and in alkaline media a series of products can be isolated in stages, viz. azoxy-, azo-, and finally hydrazo-benzene. If sodium in methyl alcohol is used, then the reduction stops at the azoxybenzene stage, and, if iron powder is used, considerable slowing down of the reduction occurs at the azo stage; in some processes, reduction is first carried out with iron to this stage, and completed by zinc to the final hydrazo product. These reactions are, in general, given by all nitro compounds.

The reduction in neutral solution is thus the penultimate stage on the route to amine, but in alkaline solution the normal course of the reduction is interrupted by an aldol condensation which takes place at a greater rate than the reduction, viz. that of the β-phenylhydroxylamine with the preceding reduction product nitrosobenzene to form azoxybenzene. This aldol condensation is strongly favoured by alkalis, and with hydroxylamine itself nitrosobenzene gives phenylnitrosoamine, i.e. the nitrosobenzene is diazotised[17].

INFLUENCE OF SUBSTITUENTS ON THE ALKALINE REDUCTION

Azoxybenzene and azoxy compounds in general are stable yellow substances, and generally require stronger reducing agents than sodium methoxide for their conversion into azo compounds. Should, however, some arylhydroxylamine escape condensation, as in the case of *o*-nitrotoluene when reduced with zinc dust in the presence of alkali, then free amine appears in the final product, e.g. *o*-toluidine accompanies the *oo'*-hydrazotoluene. Electronic considerations indicate that the anionoid methyl substituent will tend to restrain the hydrogen atom from leaving the nitrogen in the *o*-toluylhydroxylamine and so *retard* the aldol condensation—



whereby partial final reduction to amine (*o*-toluidine) is facilitated; correspondingly, kationoid substituents, e.g. alkoxy groups, will promote the aldol condensation. Energetic alkaline reducing agents such as ferrous oxide (ferrous sulphate and ammonia) yield amines direct, while electrolytic reduction can be adjusted so that it ceases at any desired stage.

REDUCTIONS BY SODIUM HYDROSULPHIDE[18]

One of the alkaline reducing agents which can take the reduction process to stages dependent on the constitution of the nitro compound treated is sodium hydrosulphide. Hodgson and Ward[19] have found that, when the three dinitrobenzenes are submitted to this reagent in aqueous methanol, the *o*-dinitrobenzene is converted almost entirely into a mixture of sodium *o*-nitrophenylthiol and 2:2'-dinitrodiphenyl monosulphide, the *m*-dinitrobenzene affords 90–95% of *m*-nitroaniline, and *p*-dinitrobenzene gives mainly *pp'*-dinitroazobenzene (> 60%) with some *pp'*-diaminoazobenzene, *p*-nitroaniline (approx. 12%), and probably *p*-phenylenediamine. The influence of the *p*-nitro group in retarding the reduction is most pronounced, and, since nitro groups are strongly kationoid and should therefore facilitate reduction by making the azo compound more kationoid, it follows that in the alkaline medium there has been some interaction between the nitro group and the methyl alcoholic alkali[20] whereby the normal kationoid character of the nitro group has been reversed to anionoid. A close parallel to this reaction is the Gomberg reaction between *p*-nitrobenzenediazonium hydroxide and *p*-nitrobenzene to form *pp'*-dinitrodiphenyl in at least 70% yield, where the kationoid effect of the nitro group in the nitrobenzene has been reversed to anionoid by the alkaline or glacial acetic acid medium employed. The *m*-nitro group can exert only a slight influence, hence the almost quantitative reduction of *m*-dinitrobenzene to *m*-nitroaniline.

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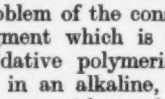
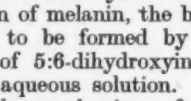
The Oxidative Dyeing of Keratinous Protein Fibres
I—The Dyeing of Wool with the Colourless 2:4:5-Trihydroxytoluene

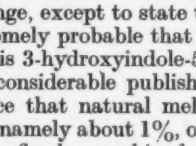
H. BURTON and J. L. STOVES

It is shown that wool fibres can be dyed various shades of brown by aqueous solutions of the colourless 2:4:5-trihydroxytoluene. Simultaneous treatment with various metal salts causes a pronounced darkening in the shade, which becomes almost black with ferrous iron. The brownish-black stain obtained by application of the trihydroxytoluene to living skin is attributed to the formation of a co-ordination complex derived from a thiohydroxytoluquinone and iron; a similar process can thus be separated into two distinct stages with wool.

We have been interested for some years[1] in the problem of the constitution of melanin, the black pigment which is known to be formed by the oxidative polymerisation of 5:6-dihydroxyindole (I) in an alkaline, dilute aqueous solution. We do not wish to discuss the mechanism of this particular change, except to state that we consider that it is extremely probable that an intermediate in the process is 3-hydroxyindole-5:6-quinone (II). There is also considerable published[2] and unpublished[3] evidence that natural melanins contain a small amount, namely about 1%, of sulphur, which appears to be firmly combined. The mode of combination of the sulphur has, so far as we are aware, never been discussed, but we consider that it could easily be incorporated into the pigment by addition of a thiol grouping RSH to (II) with subsequent oxidation of the intermediate 5:6-diol to the compound (III). In turn, this would be incorporated into the "polymerised molecule" of the natural melanin. It is difficult to study the


(I)

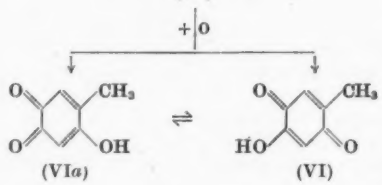

(II)

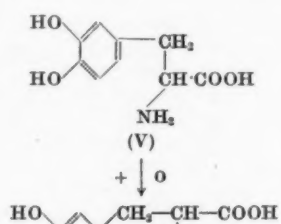

(III)

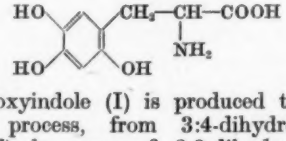
oxidative changes of (I) in the presence of thiols since, in an alkaline medium, the conversion of (I) into melanin is extremely rapid. We were of the opinion, however, that some light on the formation of pigments* could be obtained from a study of compounds related structurally to (I).

In view of the foregoing considerations we decided to study the behaviour of 2:4:5-trihydroxytoluene (IV), and since our reasons for selecting this *nitrogen-free* compound may not be immediately apparent, we should like to explain our choice of this particular compound for further study. It is known from the work of Raper[4] that

(IV)


(VI*a*) (VI)


(V)

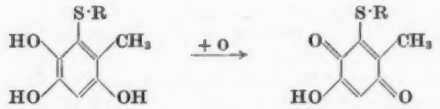


5:6-dihydroxyindole (I) is produced through an oxidation process, from 3:4-dihydroxyphenylalanine (V) by way of 2:3-dihydroindole-5:6-quinone-2-carboxylic acid. Assuming that oxidation of (V) can be effected in the benzene nucleus as shown, it is impossible for indole ring formation to occur. The amino-acid side-chain, although containing nitrogen, is now clearly of relatively little importance, and the simplest and most readily accessible prototype of this is clearly (IV). Oxidation of (IV) is known[5] to give (VI). We should like to point out that the corresponding

* *Not* melanins. We restrict the use of *melanins* to the pigments produced from 5:6-dihydroxyindole and its derivatives.

o-quinone (VI*a*) might equally well be produced by oxidation of (IV); the compounds (VI) and (VI*a*) are, in fact, tautomeric substances, but it is clear from the work of Thiele and Winter[5] that (VI) is the stable form. These authors state that solutions of (IV) in alkali give the red alkali-metal salt of (VI). We have found that this oxidation occurs readily in any dilute alkali (e.g. dilute ammonia or even tap-water) and traces of (IV) can be immediately detected. Solutions in distilled water are, of course, slightly acidic, a 0·5% solution of the pure, colourless (IV) having a pH of 4·8. Such solutions develop an orange to pinkish-orange tint when kept in air.

Quinones of type (VI) can readily add a molecule of a thiol, producing, for example, the trihydroxytolyl sulphide (VII), which, in turn, can be oxidised to the corresponding sulphur-containing quinone (VIII)—



(VII) (VIII)

We also considered it to be extremely probable that the trihydroxytoluene, since it can be readily oxidised, might function as a reducing agent towards the disulphide group—

$$(IV) + RS{\cdot}SR \rightarrow (VI) + 2\,RSH$$

If this reaction occurred to any extent, then clearly it should be possible for the reaction—

$$(VI) + RSH \rightarrow (VII)$$

to occur.

Accordingly, we first studied the effect of (IV) on our own skin, which as a keratinous protein contains the necessary R·S·S·R grouping. We made no attempts to exclude oxygen, as we required two oxidations to supervene after the formation of (VII), namely the reoxidation of the second R·SH molecule to regenerate disulphide and the conversion of (VII), which must be colourless, to (VIII), which must be coloured, and must also be combined (through the group R) with the protein. The possibility of introducing a second SR group into (VIII) by a repetition of the process is not, of course, excluded; neither is the oxidation–reduction reaction of (VII) with (VI) to give (IV) and (VIII). We found, on applying a dilute aqueous solution of (IV) to any part of the skin, that a stain developed slowly: the colour increased in intensity with time, and ultimately became brownish-black (see Fig. 1). We realise that under these conditions some or all of (IV) may have been oxidised to (VI)— in fact a "quinone smell" at the site of the application was noticed— and that this may have reacted with possible SH groups in the skin protein. We do not think that the latter explanation is the real one, since application of an alkaline solution of (IV), and hence (VI), caused no staining at all.

The colour of the stain appeared to be too black for a quinonoid structure, which we should have

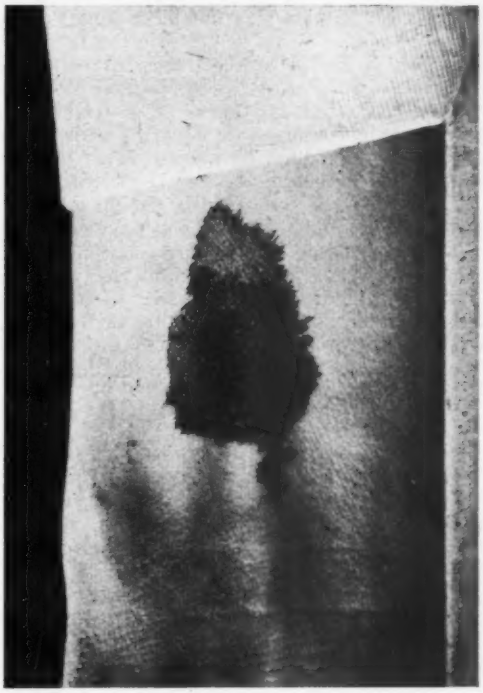


FIG. 1

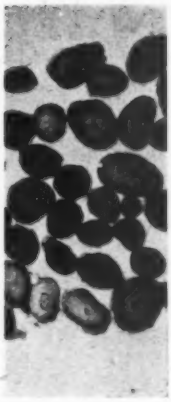
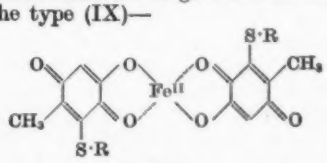


FIG. 2

expected to give some shade of brown. We therefore presumed that iron, present in the skin or in the blood supply to the skin, was being incorporated into the final structure to give a co-ordinated iron salt of the type (IX)—



(IX)

Our subsequent work indicates that this is probably the correct explanation of the intense colour,

although the reaction may not be as simple as we have suggested.

We then investigated the dyeing properties of (IV) towards wool, since the two stages— (i) formation of (VIII), (ii) formation of (IX)— can clearly be separated. As expected, stage (i) leads to the production of reddish-brown to light medium brown dyeings according to the pH of the solution. The darkening in colour with rise in pH may appear, at first sight, to be anomalous: especially since we have stated that alkaline solutions of (IV) do not stain skin. We do not think that this is so for the following reasons. Increase in the alkalinity of the solution will clearly facilitate the oxidation of (IV) to the quinone, but at the same time will cause the known fission of the S·S linking to give –SH; accordingly the reaction—

$$\text{(VI)} + \text{RSH} \rightarrow \text{(VII)}$$

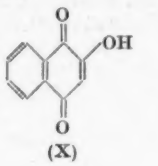
will be facilitated by hydroxyl ions (degradation of the fibre is, of course, concurrent). We should expect, therefore, that for a given weight of fibre, an increase in pH would be accompanied by an increase in the amount of (IV) used: we consider that our results prove that this is so.

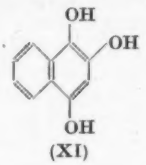
It will be apparent from our mode of formulation of the dyeing process that some of the original S·S linkings of the fibre have been combined with benzene nuclei. We should, accordingly, expect the fibre to have been strengthened at the lower pH values. The load–extension curves (see Experimental Section) appear to prove that such is the case.

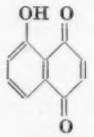
The only alternative to the formation of sulphide linkings in the dyed fibres is that free amino groups of the protein molecule react with the quinone to form, ultimately, a substituted aminoquinone. This type of reaction appears to us to be unlikely, and the supercontraction values[6] of treated and untreated hair indicate that this type of reaction has not occurred.

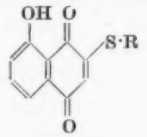
We have suggested (above) that the dark stain produced on living skin by (IV) is due to the incorporation of iron into the molecule. Dyeings carried out with 0·5% solutions of (IV) to which 1% of crystalline ferrous ammonium sulphate was added gave a black shade. The dyeing was not absolutely uniform, and occasional fibres, when examined under a lens, showed a dark brown tint. The penetration of the trihydroxytoluene into the original fibres is probably not completely uniform, and this appears to be substantiated by the photomicrograph (Fig. 2) of the "black" fibres. Results with other metal salts show that iron is the only one of the metals so far investigated to give a black colour, although copper similarly produces a dark brown shade.

It was not until we had carried out the work described above that we realised that the orientation of the hydroxyl and quinone groups was the same in (VI) as in lawsone, the yellow pigment from henna leaves. Lawsone (2-hydroxy-1:4-naphthaquinone) (X) is known to be readily produced by oxidation of 1:2:4-trihydroxynaphthalene (XI), especially in the presence of alkali. It will dye wool and silk a bright orange from an acid bath[7]. The possibility that (XI), *provided it did not undergo rapid atmospheric oxidation to* (X), would behave similarly to (IV), was clearly worth investigating. Our results show that oxidation does occur rapidly


(X)


(XI)


(XII)


(XIII)

when (XI) is applied to the skin, but not when wool is treated with an aqueous solution.

1:2:4-Trihydroxybenzene (hydroxyquinol), as expected, resembles (IV) in its behaviour. We attach some importance to this similarity, since an alternative mode of oxidation of 3:4-dihydroxyphenylalanine is the elimination of the amino-acid side-chain and its replacement by a hydroxyl group. The resulting product would thus be 1:2:4-trihydroxybenzene.

5(8) - Hydroxy - 1 : 4 - naphthaquinone (juglone) (XII), which is isomeric with lawsone, also exhibits an interesting "dyeing property" towards skin: it is stated[8] that its colourless hydro derivative undergoes rapid oxidation on exposure to air, and the resulting quinone produces stains on the skin, probably in consequence of the addition of the quinone itself to active groups of the protein. We attribute this behaviour to the reactions described above for (IV) in the presence of iron, since the resulting thiohydroxynaphthaquinone (e.g. XIII) could form a chelated iron salt through the OH group and the O in the *peri* position.

Experimental

Human hair of known origin was extracted with ether and alcohol in a Soxhlet apparatus. This treatment was followed by washing in distilled water, the fibres being finally dried between filter papers. The change in ease of extensibility of these fibres after treatment with 2:4:5-trihydroxytoluene was estimated from the load–extension curves, which were determined by means of a balance-type extensometer. In each case, a 5-cm. length of the root part of the fibre was attached by means of sealing wax to light glass hooks, and calibrated by determining its load–extension curve in distilled water at 22·2°c. After standing overnight in distilled water, the fibre was treated with 20 c.c. of the reagent maintained at a constant temperature in an air thermostat. This treatment was followed by washing in running water for 48 hr., and the load–extension curve was then redetermined. Extension was in each case limited to 30%, and from the curves the difference in work required to perform a 30% extension was calculated and expressed as a percentage of the work required for the original 30% elongation.

In certain cases the supercontraction of fibres in sodium metabisulphite was examined. Loose fibres were boiled under reflux for one hour with 5% sodium metabisulphite solution containing 5% of ethyl alcohol as an antioxidant. After 5 min. washing in cold distilled water, the fibres were dried singly in the absence of tension. This operation was carried out by allowing the fibre, held at one end in forceps, to hang freely in the convection current from an electric lamp.

REACTION OF HUMAN HAIR WITH 0·2 M. 2:4:5-TRIHYDROXYTOLUENE

Human hair fibres were calibrated by stretching in water as previously described, after which they were treated for 72 hr. at 40°C. with 0·2 M. aqueous solutions of 2:4:5-trihydroxytoluene, buffered to pH 1 and 4 with Walpole sodium acetate–hydrochloric acid buffers. The load–extension curves of the treated fibres were then redetermined and the percentage change in work was calculated. Blank experiments were performed using buffer solutions alone. Results are given in Table I.

TABLE I

pH	Change in Work (%)— 2:4:5-Trihydroxytoluene	Buffer only
1·0	+ 1·9	− 5·8
4·0	+ 12·0	− 1·4

The differences between the treated fibres and the corresponding blanks, viz. 7·7% and 13·4% change in work, show that reaction has taken place leading to the formation of new linkages between the polypeptide chains of the keratin fibres. The question arises as to which polypeptide side-chains are involved in the linkage formation.

Now when normal fibres, whose load–extension curves have been determined in the normal manner, are allowed to stand for 17 hr. in 0·1 N. hydrochloric acid, and then restretched in the acid, they are found to suffer a 30% reduction in work. This increased ease of extensibility is attributed to complete rupture of salt linkages having taken place. This fact was used to examine the extent to which amino groups of salt linkages are taking part in the reaction of fibres with trihydroxytoluene. The fibres used for the experiments reported in Table I were allowed to stand overnight in 0·1 N. hydrochloric acid at 22·2°C. and then restretched in the acid. Table II gives the results

TABLE II

pH of Treatment	Change in Work in 0·1 N-HCl (%)— Treated Fibre	Untreated Fibre
1·0	− 28·0	− 30·6
4·0	− 28·0	− 32·3

obtained, and shows that in fibres treated for 72 hr. at 40°C. with 0·2 M. aqueous solutions of pH 1 or 4, salt linkages are involved to a very limited extent, if at all.

The supercontraction of the treated fibres should be less than that of fibres treated with buffer solutions alone. The figures for fibres treated for 72 hr. at 40°C. with a 0·2 M. solution of trihydroxytoluene and with buffer alone are 24·5% and 29·3% respectively, while for fibres treated for 1 hr. under reflux the results are 20·5% and 30·4%. Hence new linkages which are stable to boiling metabisulphite are formed during treatment of hair with 2:4:5-trihydroxytoluene of pH 4 at 40° or 100°C. This observation does not prove that the linkages involve thiol groups, but such a view seems reasonable.

DYEING PROPERTIES OF 2:4:5-TRIHYDROXYTOLUENE

The dark stain produced on living skin by 2:4:5-trihydroxytoluene suggested the desirability of examining the colours produced by the compound on normal and mordanted wool. Accordingly, samples of solvent-extracted Cotswold wool were treated for 1 hr. at 90°C. with 0·5% aqueous solutions of 2:4:5-trihydroxytoluene (pH 4·8 unbuffered) alone and in the presence of 1% of a metallic sulphate. The concentrations given are those of the actual solutions and are not calculated on the weight of wool. A 30 : 1 liquor : wool ratio was used. The samples were scoured with soap and water, washed in running water, and dried, with the results shown in Table III.

TABLE III

Conditions of Treatment with 2:4:5-Trihydroxytoluene	Colour of Wool
pH 3	Light reddish brown
pH 4·8	Medium brown
pH 9	Darker brown
+ Cupric sulphate*	Very dark brown or black
+ Ferrous ammonium sulphate* ...	Black
+ Cobalt ammonium sulphate* ...	Medium brown

* AR crystals

APPENDIX

Rubbing Fastness of Dyeings

Since this paper was submitted for publication, the rubbing fastness of the wool dyed with 2:4:5-trihydroxytoluene has been tested by Dr. C. B. Stevens of Leeds University, to whom the authors wish to express their thanks.

Samples of the material were tested according to a method devised by the Wool Industries Research Association using the W.I.R.A. Rubbing Tester (by permission of Dr. F. F. Elsworth). Details of the test used were as folllows—

Number of rubs	...	50
Length of stroke	...	4·25 in.
Load	...	3·6 lb./sq. in.

A reference sample of material similar to that submitted for testing was dyed with 3% Solochrome Brown RHS (ICI) using the afterchrome method. Chroming was carried out in a fresh bath using 1·5% potassium dichromate. The reference sample was tested in the same way as the other samples.

TABLE IV

Rubbing Fastness Tests

(All dyeings in a 30-vol. 0·5% aqueous solution of 2:4:5-trihydroxytoluene for 90 min. at 90°C.)

Sample	Addition to Dyebath	Appearance of White Cotton Sateen used for Rubbings
1	—	Lighter than with reference sample
2	0·5% Teepol (Shell) ...	As Sample 1
3	1% Ferrous ammonium sulphate	Very slightly darker than with reference sample

In all cases, the amount of staining was only slight, and the fastness of the samples to dry rubbing is considered to be satisfactory.

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The Application of Vat Dyes to Wool and Wool–Rayon Staple Mixtures

R. C. CHEETHAM

It is well known that difficulties are encountered when vat dyes are applied to animal fibres by normal methods chiefly owing to the loss of tensile strength due to the fibres being attacked by the alkaline liquors. In addition, when animal fibres are found in admixture with cellulosic fibres, it is often desirable to obtain solid shades on both types of fibres with vat dyes. In this paper methods are suggested for achieving both these aims by incorporating sodium metadisilicate in the alkaline reducing liquor, and then adding sodium bisulphate to reduce alkalinity and secure solidity of shade. The procedure may also be adopted for the dyeing of wool alone with all classes of vat dyes provided the leuco compound is sufficiently soluble.

The method of calculating the required amount of sodium bisulphate is described, and attempts are made to show how sodium silicate contributes to the efficiency of the process.

Light and washing fastness tests have been carried out, the results indicating, in general, that normal fastness standards are maintained.

Introduction

The fastness demands of tropical suitings, made wholly of rayon staple fibre, implying dyes with light and washing fastness of a high order, are satisfied by the use of vat dyes. Since it is becoming the practice to include a proportion of wool in the blend for this particular purpose, it was considered desirable to investigate the application of vat dyes to blended yarns of wool and Fibro, and if possible to provide a method for the production of solid shades on such blends. There are two major difficulties in the way of this objective: firstly, under any known fixed conditions of dyeing, it is likely that vat dyes in general will have different affinities and/or absorption rates on the two fibres. Secondly, any method of dyeing must take into account the deleterious effect on wool of the relatively strongly alkaline dyebaths normally used with vat dyes. This effect is due to the partial breakdown of the cystine linkages, which contribute so much to the structural stability of the fibre. Fibre weakening is particularly liable to develop with sodium hydroxide[1], so that when wool is dyed in the normal manner with vat dyes it is practically impossible to avoid disulphide bond breakdown, characterised by such defects as reduction in tensile strength and loss of felting power.

Table I illustrates the degree of damage in terms of percentage loss in strength of 2/24's worsted yarn for some typical vat dye liquors. These figures can be compared with the effect of a chrome blue dyed by the chromate process on the same kind of yarn, which shows a reduction in strength of 8·7% after one hour's boil.

It will be clear from Table I that a concentration of caustic soda exceeding 2·15 g./litre would cause appreciable damage to wool.

TABLE I

Reduction in Strength of 2/24's Worsted Yarn dyed with Vat Dyes at 60°C. for 30 min.

Dye	Alkalinity (g. NaOH per litre)	Reduction in Strength (%)
Paradone Jade Green XS (LBH) ...	5·4	40
Caledon Blue RCS (ICI)	5·4	40
Caledon Gold Orange 3GS (ICI) ...	4·3	29
Paradone Red Brown 5RD (LBH) ...	4·3	28
Caledon Brown RS (ICI)	2·15	19

The degradation of the wool fibre may be minimised but not entirely eliminated by the use of colloidal substances such as glue, sulphite waste liquors, and the like[2].

The attack is aggravated by the need to maintain a sufficiently strong alkaline liquor to preserve the solubility of the leuco compounds during dyeing; this alkali is in practice considerably in excess of the theoretical requirements for the formation of sodium leuco compounds It was found that the amount of sodium hydroxide could be reduced substantially below the quantities recommended in manufacturers' pattern cards and it was still possible to obtain good leuco vats.

One method of partly overcoming the deleterious action of caustic alkali on protein fibre is the employment of alternative alkalis; a number of such alkalis have been suggested from time to time, but in general they are found to have only a limited value. Sodium hexametaphosphate[3] has been used to some effect with those dyes which give leuco compounds of good solubility in this medium, and it is possible to employ sodium metasilicate in some cases, whilst sodium carbonate is satisfactory for a limited range of dyes. It was concluded that no success in this direction was possible over an extended range of vat dyes, and attention was directed towards an entirely different method based on a partial or complete neutralisation of the caustic alkali after vatting.

Experimental

In the case of many vat dyes in the "weak alkali" class it was found possible to reduce the recommended amount of caustic soda by half and make up the deficiency in terms of alkalinity by adding sodium silicate; this procedure was possible without causing a significant increase in damage to the wool when subsequently dyed. Further points of practical importance noted when sodium silicate was used included good dispersion of vat dye particles prior to reduction and a lower degree of flocculation.

The exact rôle played by the silicate from a chemical point of view has not yet been established. It is possible that particles of colloidal silica, of which sodium silicate is partly composed, are absorbed by the wool and so exert a protective influence.

Various brands of sodium silicate were examined with a view to deciding on the one giving optimum results. It is known that sodium silicate is a general term for a number of compounds derived from or containing silica, and the exact chemical constitution is in many cases difficult to define. The compound known as sodium metasilicate is Na_2O,SiO_2 or Na_2SiO_3; it exists in the crystalline state and the solution in water is strongly alkaline. The compound $Na_2O,2SiO_2$, sodium metadisilicate, is the commercial "water glass", and this was used in most of the experiments. Silicates containing higher ratios of silica to sodium oxide are regarded as colloidal systems of silica in a solution of sodium metasilicate or of sodium metadisilicate. There are grades with a silica : sodium oxide ratio as high as 3·4 : 1, and such a product may be represented as $Na_2O,3{\cdot}4SiO_2$ as a convenient form of notation. The latter is one of the least alkaline forms of silicate and liberates a high proportion of silicic acid, and ultimately silica, when acted upon by an acid or acidic substance. This brand was found to be too unstable for general purposes. The different brands of silicate vary somewhat, the most alkaline form being approximately four times as strong a base as the least alkaline. They are all less alkaline than caustic soda.

Although fibre strength could clearly be maintained during vat dyeing by the use of caustic soda–silicate baths, the relative affinity of wool for leuco compounds compared with that of Fibro was not usefully influenced. It was, however, apparent that less alkaline conditions favoured increased absorption of dye by wool.

With the object of further reducing alkalinity, experiments were carried out with various acids and acid salts. It was observed that, although acids were very effective agents for attaining this objective, they tended to reduce alkalinity too rapidly and consequently increased the tendency for dyes to be precipitated, and at the same time the control of absorption was difficult. It was found that when an acid salt, preferably sodium bisulphate, is added to the leuco vat, a means is provided of reducing alkalinity and simultaneously increasing the affinity of wool for the leuco compound; there is also an appreciable reduction in percentage loss in strength of the wool fibres.

One of the advantages of sodium bisulphate over other acid salts is that sodium sulphate is produced in the dyebath, and this has beneficial results as a dyeing assistant for wool and in many cases for Fibro as well.

Table II shows the percentage reduction in strength of worsted yarn when dyed in a similar manner to the examples in Table I with the addition of sodium bisulphate to the leuco vat dyebaths.

TABLE II

Dye	Alkalinity (g. NaOH per litre)	Sodium Bisulphate (g./litre)	Reduction in Strength (%)
Paradone Jade Green XS ...	5·4	5	33
Paradone Jade Green XS ...	5·4	16	20
Caledon Brown RS ...	2·15	5	7

In order to secure maximum protein fibre strength the vat dye was reduced according to the method described earlier involving minimum caustic soda and the incorporation of a silicate of soda such as the metadisilicate, the dyeing conditions otherwise being normal. The vatted dye was diluted to full dyebath volume, the sodium bisulphate solution then added slowly with stirring to avoid local precipitation, and the material consisting of wool and cellulosic fibre such as Fibro afterwards entered. Dyeing was for 30 min. at 60°C. Invariably the colour of the vat was altered by the acid salt, and with increasing amounts of the latter the dyebath gradually assumed the colour of the acid leuco compound. Thus, in the case of Paradone Jade Green XS the colour of the vat changed from blue (alkaline leuco compound) to a violet, then mauve, and finally red (acid leuco compound). The normal shade of the parent vat dye returned on oxidation, but in most cases the time required for the wool to assume normal shade was substantially longer than for the Fibro. The dyeing of Caledon Red BNS was particularly resistant to air oxidation, and a quicker result was obtained by treatment with 0·5% potassium persulphate at 70°C. for 20 min.

As the addition of sodium bisulphate was increased so the absorption of leuco compound by the wool increased, whilst absorption by the Fibro correspondingly decreased, and the two fibres thus approached more nearly solidity of shade; solidity was achieved in some cases at a point not far distant from total conversion of alkaline to acid leuco compound. Thereafter the absorption by the wool continued to increase to such an extent that in some cases the wool was dyed and the Fibro was practically reserved, until a critical point ensued and a reduced affinity was apparent on both fibres; this was consonant with a fall in pH below 7 and was accompanied in most cases by precipitation. The amount of acid salt used depends on the individual dye and on the alkalinity of the vat, and should be such as to confer enhanced dyeing affinity on the animal fibres to such an extent that there is equal depth of shade on both animal and cellulosic fibres. The exact amount is decided by preparing graphs showing the depth of shade plotted against amount of acid salt. The data for the graphs are obtained by carrying out a series of dyeings on a mixture of wool and Fibro yarns, in whatever proportions they are ultimately to be

dyed, using dyebaths containing different amounts of sodium bisulphate. The resultant depth of shade on each fibre is estimated visually against a set of standard dyeings of known depth, expressed as percentage strength of dye.

In each of the examples shown (Fig. 1–3) the two graphs represent the course of the changes in depth of shade on Fibro and wool respectively as increasing quantities of sodium bisulphate are employed. The point of intersection represents equal depth of shade on the two types of fibre. The upper graph slopes fairly sharply through the solidity point, and if it be then extended to intersect the abscissæ, the point of intersection will represent approximately the amount of sodium bisulphate required to convert the alkaline leuco compound wholly to the acid derivative or the so-called acid leuco compound. The lower graph, after intersection, proceeds to a peak and then descends fairly rapidly (not shown), the gradient being not quite so steep as that of the Fibro graph. Reduced affinity on both fibres is connected with the lower solubility of the leuco compound at lower pH values.

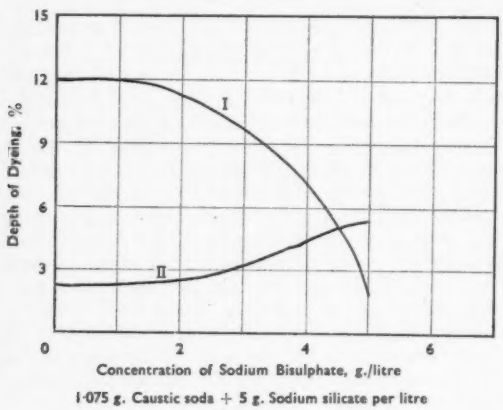


FIG. 1— Relative Dyeing Affinities of Fibro and Wool for Caledon Brown RS paste

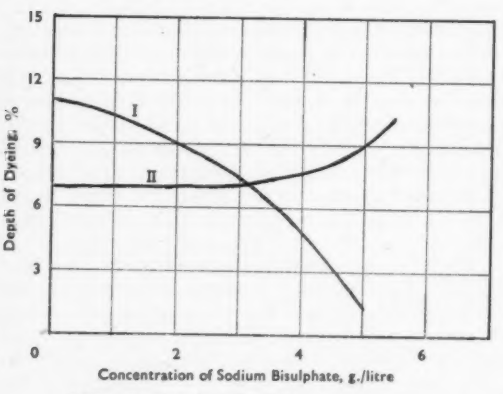


FIG. 2— Relative Dyeing Affinities of Fibro and Wool for Caledon Navy Blue 2RS paste

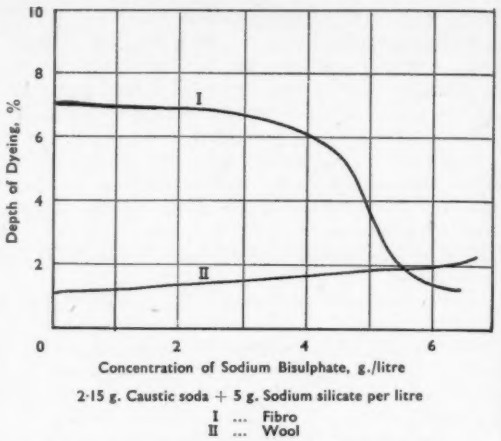


FIG. 3— Relative Dyeing Affinities of Fibro and Wool for Caledon Olive R 300 powder

The slower oxidation of the leuco compound on the wool fibre is probably due to preferential absorption of acid leuco compound, more difficult to oxidise, or possibly to a partial formation of acid leuco compound *in situ* by combination with carboxyl groups of the keratin molecule, even without the intervention of an acid salt; without the acid salt the extent of formation of acid leuco derivative is not likely to be very great.

It seems likely that through the agency of an acid salt the vat dyebath is transformed into a mixture of both alkaline and acid leuco compounds. When material composed of both animal and cellulosic fibres is entered into such a dyebath selective dyeing takes place, the cellulosic component absorbing alkaline leuco compound in the normal way, and the animal component combining with acid leuco compound, primarily by virtue of basic groups but also simultaneously by combination of alkaline leuco compound with carboxyl groups. It is not suggested that these reactions account for the whole of the wool dyeing process, for when various vat dyes are considered, the form of the graphs suggests that individual dyes vary between fairly wide limits in the amount of sodium bisulphate necessary to effect solid shades, irrespective of whether or not they fall in the same general class as regards alkali requirements. In general it has been found that the amount of sodium bisulphate which may usefully be added to the dyebath must be not only sufficient to ensure that wool fibre degradation is at a minimum but should be adequate to promote dyeing of both the wool and the Fibro to such an extent that the percentage depth of shade on both fibres is substantially the same. The dyes which are applicable include both anthraquinonoid and indigoid types. The practical quantities of sodium bisulphate vary from about 3 g. to about 16 g. per litre of dye liquor, and dyes of both "weak" and "strong" alkali classes as well as indigoid types are found within this range of values. The minimum for any particular dye is that quantity below which no advantage is conferred from the point of view

of reduction in degradation of wool protein, and the maximum is defined as the quantity above which the resultant fall in pH would be such as to reduce the solubility of the leuco compound and would result in dyeings of abnormally low strength.

This range of values can also be interpreted to mean that the larger amounts are used for dyes requiring a strongly alkaline vat, and the smaller amounts are added to weakly alkaline vats or to vats in which the caustic soda has been partly replaced by a sodium silicate in order to reduce total alkalinity.

EFFECT ON P_H OF PROGRESSIVE ADDITION OF SODIUM BISULPHATE

In order to correlate dyebath pH with added sodium bisulphate, a more detailed study was undertaken of one particular anthraquinone vat dye. The dye chosen was Caledon Red BNS paste, this being selected partly because the procedure described above is applicable and also on account of the distinctive colour changes from alkaline to acid leuco conditions.

Small-scale dyebaths were prepared on the basis of a 16% dyeing on 5 g. of material in 40 volumes. The concentration of dye was purely arbitrary, but was intended to be sufficient to exert an influence on dyebath pH, so that a comparison could be made between the dyebaths with and without dye.

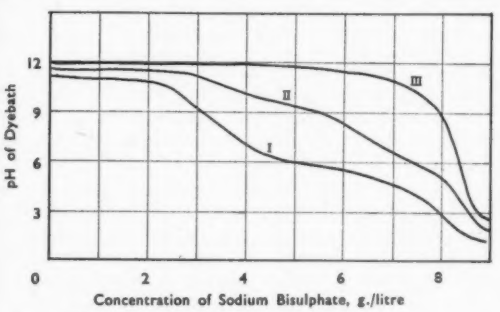
The dyebaths were as follows—

(1) As described above, using 2·15 g. caustic soda per litre and 10% sodium hydrosulphite (on weight of material) for vatting.

(2) As above, using 1·075 g. caustic soda and 5 g. sodium metadisilicate per litre, and 10% sodium hydrosulphite (on weight of material) for vatting.

(3) A blank dyebath containing 2·15 g. caustic soda per litre and 10% sodium hydrosulphite (on weight of material).

Small portions of sodium bisulphate (10% solution) were added progressively, and the pH noted after each addition. Fig. 4 illustrates the results,



I ... 2·15 g. Caustic soda per litre + dye
II ... 1·075 g. Caustic soda + 5 g. sodium silicate per litre + dye
III ... 2·15 g. Caustic soda per litre (blank dyebath)

FIG. 4— Effect on pH of Caledon Red BNS (paste) Dyebath of Progressive Addition of Sodium Bisulphate in the Absence of Material

and reveals the course of the fall in pH caused by the addition of an acid salt during the formation of an acid leuco compound. Since there is no material in these dyebaths and consequently no actual dyeing taking place, there is no reason to believe that results for other dyes would differ materially from those for Caledon Red BNS, provided the solubilities of the corresponding leuco compounds are similar. This view was confirmed when the above series of experiments was repeated with Paradone Jade Green X 300 paste.

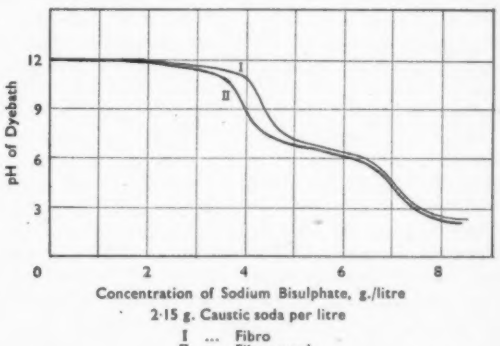
The first graph shows a fairly sharp fall as the formation of acid leuco compound nears completion, remaining steady for a time before falling rapidly below pH 6, as the hydrosulphite is decomposed.

In the case of the second graph there is little change initially, and then there is a fall, not however so sharply defined as in the first graph; thereafter the graph follows a similar course to the first graph.

The third graph, representing the blank dyebath, is a simple illustration of the titration of an alkali with an acid salt.

The inclusion of sodium silicate is clearly beneficial, since on the addition of sodium bisulphate a steady fall in pH is registered, particularly in what would be the absorptive range for dyeing. The course of the graphs below pH 6 is not of interest from a dyeing point of view, since decomposition of sodium hydrosulphite commences around this value and precipitation ensues within a very short time. Incidentally, it was found advantageous on occasions to add a further small amount of sodium hydrosulphite in the early stages of dyeing to guard against the possibility of precipitation due to a fall in reducing power of the dye liquor, which is obviously a more likely occurrence at pH values approaching 7.

These progressive additions of sodium bisulphate were repeated with material in the dyebath, in the one case with 2/20's Fibro and in another with an equivalent weight of a mixture of fibres containing equal proportions of 2/20's Fibro and 2/24's worsted. The blank dyebath was omitted in this experiment. Dyeing was conducted at 20°C. in 40 volumes in stoppered conical flasks under otherwise normal dyeing conditions. No salt or any auxiliary product was used. The results are shown in Fig. 5 and 6, and follow the same general lines as in Fig. 4. The amount of sodium bisulphate required to produce the changes in composition of the leuco vat is slightly less when wool is present, probably owing to absorption of sodium hydroxide by the



I ... Fibro
II ... Fibro–wool

FIG. 5— Effect on pH of Caledon Red BNS (paste) Dyebath of Progressive Addition of Sodium Bisulphate in the Presence of Material

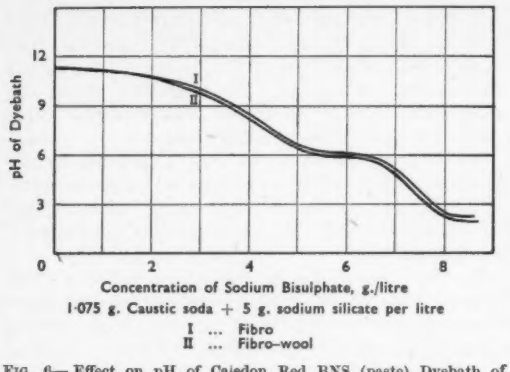


FIG. 6— Effect on pH of Caledon Red BNS (paste) Dyebath of Progressive Addition of Sodium Bisulphate in the Presence of Material

wool fibre with consequent fall in alkalinity. It will be noted, however, that this difference in reactivity is not pronounced in the presence of sodium silicate, and this may indicate the "protective" action of sodium silicate, or more correctly of the silicic acid or silica, towards the wool fibre (p. 479).

APPLICATION TO WOOL

The process is equally applicable to wool alone, and some dyes have been found to be particularly suitable from the point of view of substantially increased depth of shade accompanied by enhanced brightness of tone. They include Caledon Red Violet 2RNS, Caledon Red BNS, and Solanthrene Orange F3R (CN).

FASTNESS PROPERTIES

In general the fastness properties of both protein and cellulosic fibres are well maintained when dyed with vat dyes under the conditions described, although some "weak alkali" dyes are slightly inferior in washing fastness when the maximum amount of sodium bisulphate is used. In practice this could be overcome by reducing the amount of sodium bisulphate, thus involving a slight sacrifice of solidity and tensile strength. A slightly lower standard of solidity on the two fibres would scarcely be noticeable in an intimately blended mixture, and where such a material is to be dealt with it is therefore not always necessary to adhere to the precise quantities indicated by the graphical method.

It is essential that preliminary tests should be carried out to obtain knowledge of the individual dyes to be used and their dyeing properties under lowered pH conditions such as are likely to be produced by the addition of sodium bisulphate.

The light fastness of vat-dyed wool is influenced by the presence of residual reducing agent after removal from the dyebath[4]. It was found that reduction in light fastness was prevented by boiling in a dilute acetic acid bath after oxidation. The addition of Lissapol C (ICI) at this stage is beneficial in maintaining the soft handle of the wool.

The author wishes to thank the Directors of Messrs. Courtaulds Ltd. for permission to publish this paper, and is also indebted to Mr. J. Boulton for advice during the course of the investigation.

COURTAULDS LTD.
RESEARCH LABORATORIES
DROYLSDEN
MANCHESTER

(*Received 28th February 1950*)

References

[1] Blackshaw, J.S.D.C., **44**, 297 (1928).
[2] I.G. Farbenindustrie A.-G., Wallis, and Virck, *U.S.P.* 1,964,934.
[3] Imperial Chemical Industries Ltd., *B.P.* 388,044.
[4] Whittaker, C. M., and Wilcock, C. C., *Dyeing with Coal-tar Dyestuffs* (London: Baillière, Tindall & Cox, 5th edition 1949), p. 167.

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

"On Reading the *Journal*"

The Editor
SIR,

It may seem a little unfair to take a speaker too seriously when he is in a deliberately expansive mood, and few readers or auditors would disagree with much of Mr. R. A. Peel's lecture "On Reading the *Journal*"[1]. No organ, if it is to reflect accurately the activities of a lively, progressive, and humane Society will attempt to limit its contents to scientific and technical papers and abstracts. We are indebted to Mr. Peel for showing how much human interest and entertainment may be obtained, mainly from the other portions of the *Journal*. In parts of his lecture, however, I feel that he expresses heresies which are dangerously attractive to some of our members, and which, if not contested, may lead to a serious decline in the value and authority of our *Journal*. The trouble seems to arise from a kind of partisan interpretation of such terms as *science*, *technology*, *theory*, *practical man*, etc. Let me admit here that, where there is evidence of a lack of sympathy between the man who is attempting to explain technical processes in terms of fundamental knowledge, and the man who must conduct these processes on an industrial scale, the fault may not lie wholly on one side. These two classes of men are essential to each other, and the Society has had much success in bringing them together, so that any widening breach between them must be avoided at all costs. May I, as one who is directly concerned neither with purely academic research, nor with large-scale production, make my contribution by enunciating a few personal articles of faith?

(1) The true explanation of industrial processes can rarely be found by observation of these processes as they are conducted in the works. Simplified, systematic, and often idealised experimental approaches are frequently necessary.

(2) In this kind of experimental approach, the exclusion of any branch of that generalised body of knowledge called science, either because its relevance is not appreciated or because there are intrinsic difficulties of study, is unprogressive and may be dangerous. *Theory* is essential.

(3) It is imposing an unnecessary and often intolerable burden upon the scientific worker, dealing as he is with concepts which, while in no way mystical or transcendental, are outside normal everyday experience, to deny him a terminology appropriate to his subject-matter.

(4) The inspiration for experimental work, and the constant check upon its validity, is ultimately to be found in the working details of technical processes. The more accurately these are observed and described, and the more thoroughly they are discussed, the better for both *practical man* and *scientist*.

Now Mr. Peel, albeit gently and courteously, voices the complaint that there is too much of the theoretical and too little of the practical in the *Journal* at the present time. I suspect that some of the material he might call theoretical is, in fact, extremely pertinent and practical, but is difficult to express in words to be found wholly in the *Oxford English Dictionary*. Let us be clear on this question of terminology. Because studies are becoming more strictly quantitative, the terminology of physics finds increasing use, and this may not be very familiar. But let any working colourist who boggles at it take some simple and familiar fact of his own, such as the constitution of *p*-nitroaniline, and attempt to describe that concisely in words found only in the dictionary.

As a member of the Publications Committee and of a Section Committee, I would fight strenuously against the exercise of any discrimination against lectures or communications on the ground that they were either too practical or too theoretical. I regard the *Journal* as an open forum for the discussion of anything concerning the tinctorial processes on whatever scale, believing that this function transcends any mere question of comfortable entertainment value. If Mr. Peel, like myself and many more, finds some of its contents hard going, should he not, after a mildly rueful "Eheu fugaces", remember that there are the coming generations to help? Most of these with whom I have to do are well up to standard.

If there should appear to be a lack of balance at the present time, the explanation is simple and highly practical. Far too few worth-while practical contributions are being made. The reason for this is another story. I do not think that this difficulty is confined to our Society and our *Journal*. The commercial technical press has to face a very similar situation. Let the balance be redressed by more of our members coming forward with practical papers which have been compiled and written with the same care and effort as may be found in many of the more characteristically theoretical ones. Do not let us exclude from our pages any contribution which contains a valid message for any member of our calling.

Yours faithfully

H. A. TURNER

DEPARTMENT OF TEXTILE CHEMISTRY
COLLEGE OF TECHNOLOGY
MANCHESTER

16th July 1950

[1] Peel, R. A., J.S.D.C., **66**, 309 (June 1950).

Dyeing History

The Editor

SIR,

A publication entitled *Annals of Manchester*, by C. H. Timperley, published by Bancks & Co., Exchange Street, Manchester, in 1839, has recently come into my possession.

It is written in chronological form, and amongst the many interesting items, a number in connection with the textile trade in general, the following two may be of interest to members of the Society—

(1) Year 1762—"The secret of dyeing Turkey Red introduced by Mr. John Wilson, of Ainsworth."

(2) Year 1777—"Green dye, for cotton, invented by Dr. R. Williams."

It is interesting to note that Knecht, Rawson, and Loewenthal[1] state— "The first Turkey Red dye works in Great Britain were probably founded in Glasgow in the year 1790", and that Horsfall and Lawrie[2] state— "It is believed that the first Turkey Red dyehouse in Britain was founded in the Vale of Leven in 1790".

One wonders what happened in the 28 years between 1762 and 1790.

Who were Mr. John Wilson and Dr. R. Williams, and what was the green dye invented by the latter?

Yours faithfully

H. HAMPSON

"CHISNALL"
6 OLD HALL LANE
WORSLEY
NEAR MANCHESTER

5th July 1950

[1] *Manual of Dyeing* (London: Charles Griffin & Co. Ltd., 9th edition 1933), p. 579.

[2] *The Dyeing of Textile Fibres* (London: Chapman & Hall Ltd., 2nd edition 1946), p. 128.

Notes

Meetings of Council and Committees August

Council— No meeting
Publications— No meeting
Colour Index Editorial Panel— 29th
Summer School— 29th
Cavalcade of Colour— 28th

The Chemical Society Research Fund

The Research Fund of the Chemical Society provides grants for the assistance of research in all branches of Chemistry, about £700 per annum being available for this purpose. Applications for grants should be submitted not later than Wednesday, 1st November 1950. Forms of application together with the regulations governing the award of grants may be obtained from the General Secretary, The Chemical Society, Burlington House, Piccadilly, London W.1.

Knitting Machinery Exhibition Leicester, 11th–21st October 1950

An international exhibition of knitting machinery and accessories will be held in October at the Granby Halls, Leicester, by Messrs. *Textile Recorder* Machinery & Accessories Exhibitions Ltd., of Old Colony House, South King Street, Manchester 2, from whom further information may be obtained.

Tercentenary of Skilbeck Brothers Ltd.

The firm of Skilbeck's, drysalters, recently celebrated its three-hundredth anniversary by a reception in the Dyers' Hall, London. The business founded in 1650 by Richard Bagnall was reconstituted by John Joseph Skilbeck in 1796. Throughout its history, which is outlined in the *Dyer* (**103**, 37 (14th July 1950)), the firm has remained in the City of London.

Yorkshire Dyeware & Chemical Co. Ltd. 130 Years in the Dyemaking Industry

This company is celebrating the jubilee of its incorporation, but two of its components were founded as makers of dyewood extracts, etc. in 1820. One of these firms, Clemons, Marshall & Carbert, was founded by a former mayor of Norwich, whose portrait hangs in the Guildhall there, and who, recognising that East Anglia and the West of England had lost to the West Riding of Yorkshire their positions as the predominant centres of the wool textile industry, transferred his business to Leeds, to a site in the appropriately named Cudbear Street that is still occupied by his firm. The other firm, Wood & Bedford, was founded by James Bedford, one of whose daughters married Prof. A. G. Perkin, the son of the discoverer of mauve, and whose son, C. S. Bedford, was the inventor of Patent Fustin (*C.I.* 237), which is made by coupling diazotised aniline with fustic extract, thus combining in the manufacture of one product both the ancient and the modern techniques of dyemaking.

In the fifty years of the company's existence there has been a great revolution in the dyes used in the textile industry. At the turn of the century redwoods, natural indigo, and cudbear formed a part of nearly every order; to-day, though a few natural dyes, notably logwood, are still required, the main products demanded of the company are synthetic dyes. A fuller account of this company's history is given in the *Dyer*, **103**, 26, 27 (14th July 1950). C. O. C.

Reports on German Industry

I.G. Farbenindustrie A.-G., Leverkusen Patent Applications relating to Tetrahydrofuran Polymers

FD 1406/49*.

Copy of *G.P.*741,478 describing the production of compounds, useful as textile assistants, plasticisers, etc., by treating tetramethylene oxide with tertiary onium salts of halogen acids or of halides whose "etherates" can form tertiary oxonium salts. There are also seven other patent applications covering additions to and modifications of this basic principle. C. O. C.

I.G. Farbenindustrie A.-G., Hoechst 3-Amino-4-methoxy-1-methylbenzene-6-sulphonic Acid and 4-Trifluoromethyl-2-nitroaniline

FD 1375/49*.

Reply in English to a questionnaire submitted by an Allied investigator in 1945 demanding full details of the manufacture of the above intermediates. C. O. C.

I.G. Farbenindustrie A.-G. 14th AKo (Azo Commission) Meeting Offenbach, 5th May 1939

Microfilms of the reports, written in German, from the various azo laboratories on the previous year's work. Titles or subjects of papers are given below—

WOLFEN

FD 305/50*.

(1) *Chrome and Acid Dyes*
(2) *Leather Dyes*
(3) *Blue–Grey Fast-to-water Polyazo Direct Dyes having 2-Hydroxynaphthalene-6-carboxylic Acid or 2-Hydroxynaphthalene-3-sulpho-6-carboxylic Acid as End Component*
(4) *Benzo Fast Copper Dyes*— Diaminoazobenzenedicarboxylic acids and mixed combinations based on tetrazotised 3:3′-dihydroxybenzidine
(5) [*Sulphuric Esters of 3-Arylamino-1-butanols as Components for Fast-to-light*] *Acetate Rayon Dyes*
(6) *Sudan Dyes* [*for Double Tone Printing*].

LEVERKUSEN

FD 306/50*.

(1) *Wool Dyes*
(2) *Cotton Dyes*
(3) *Diazo Browns*— on the basis of the copper complex of—
o-Aminophenolsulphonic acid→Resorcinol
(4) *Metallisable Cotton Dyes*
(5) *Navy Blues supplementary to Benzo Fast Copper Blue FBL*
(6) *Non-gelatinising Benzo Fast Copper Brown*
(7) *Work done in the* [*Leverkusen*] *Azo Laboratory.*

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

LUDWIGSHAFEN

FD 307/50*.

(1) *Water-soluble Acetate Rayon Dyes*
(2) *Zapon Fast Dyes*
(3) [*Direct*] *Cotton Dyes*— of good fastness to light and high fastness to wet processing
(4) *Water-insoluble Dyes for Acetate Rayon*
(5) [*Black*] *Dyes for Wool*—

p-Aminoacetophenone $\xrightarrow{\text{Alkali}}$ H acid $\xleftarrow{\text{Acid}}$ *p*-Nitroaniline
(and *p*-Aminobutyrophenone)

(6) *Leather Dyes*— Green and bordeaux Erganil dyes fast to washing and acids.

MAINKUR

FD 308/50*.

(1) *Acyl Derivatives of 1-Amino-7-naphthol-3(or 4)-sulphonic Acid*— Diamond Grey GL is 6-chloro-2-amino-phenol→carbethoxy-1-amino-7-naphthol-3-sulphonic acid
(2) *Aryl and Alkyl Derivatives of 1-Amino-7-naphthol-3(or 4)-sulphonic Acid*
(3) *Neutral-dyeing Acid Dyes from* cyclo*Hexylcapryl*-p-*phenylenediamine*
(5) *Neutral-dyeing Wool Dyes*
(6) *Chlorantine Fast Yellows*
(7) *Acylated Benzidinemonosulphonic Acids as Intermediates for Azo Dyes*
(8) *Copper-complex Dyes from Aminotriazoles.*

HOECHST

FD 309/50*.

(1) *Dyes having Carbolan Properties*
(2) *Pigments from Aminoarylcarboxylic Acids*
(3) *Azo Pigments from 6-Chloro-2-toluidine*
(4) *Relation between Particle Size and Covering Power* [*of Helio Bordeaux BL, Glazing Helio Bordeaux, and Pigment Lake Red LC*]
(5) *Influence of Temperature in the Production of Pigments*— Hansa Yellow 3R and Pigment Fast Yellow 45749
(6) *Lithol Fast Scarlet RN*
(7) p-*Nitrophenylmethylpyrazolone in Azo Pigments*
(8) *Unsymmetrical Pigments from Diarylamines, β-Naphthol, and Pyrazolone*
(9) *Lithosol Yellow and Pigments from Acetoaceto-*m(*and* p)-*nitroanilide*
(10) *45 Aminoacetoacetic Acid Derivatives*
(11) *Cupriferous Direct Cotton Dyes suitable for After-treatment on the Fibre with Chromic Fluoride*
(12) *Diazotisable Dyes for Aftercoppering*
(13) *Dyes for Mixtures of Wool and Viscose Rayon*
(14) *Green Dye for Wool and Cotton*
(15) *Benzo Fast Copper and Benzo Chrome Dyes from Bispyrazolones*
(16) *Yellow Autazol and Diazotisable Dyes*
(17) *Direct Azo Dyes from Intermediates containing Aliphatically Bound Sulpho Groups.* C. O. C.

Friedrich Alexander Universität, Erlangen
Constitution of Pyrrole Blue

H. Wilhelm. FD 2181/49* (PB 73,406).

Microfilm of a doctoral thesis (pp. 25), written in German in 1940. C. O. C.

Günther Wagner Chemisches Werk, Hannover
Index to the Firm's Paints, Colours, Cements, Adhesives, and Other Products, with Notes on the Methods used in preparing them

FDX 839* (PB 74,934; Microfilm W 57).

Microfilm of 1200 pp. of records dating 1934–43 of the products made by this firm and the manufacturing processes used. They include colours for water and oil paints, printing and other inks, crayons and pencils, artists' oil and water colours, etc. C. O. C.

I.G. Farbenindustrie A.-G., Franfurt-am-Main
German Dyeing Practice

FD 574/50* (PB 13,555).

Microfilm of a speech (8 pp.), given on 22nd Feb. 1946, by the leader of a team of Allied investigators into German dyeing practice with special reference to the I.G. C. O. C.

German Textile Processing and Equipment
Cotton and Rayon Dyeing, Drying, Printing, Ageing, Steaming, Print Washing, and Finishing

FD 535/50* (PB 1573).

Microfilm of a 24-pp. report, written in English in 1945 by an Allied investigator. The preparation, dyeing, and drying of cotton and rayon cloths are described, and this is followed by a detailed review of their printing. A copy of a patent is given in which textiles are treated with dyes or finishing agents and then passed through molten metal at 125°c. C. O. C.

Textile Printing Industry in Germany

FD 154/50* (PB 13,556).

A 6-pp. report, written in 1946 by an Allied investigator, dealing with information gained at I.G.–Hoechst, at the model spinning mill at Denkendorf, and from various works. It should be read in conjunction with *BIOS* 1088 (cf. J.S.D.C., **63**, 185 (1947)). C. O. C.

I.G. Farbenindustrie A.-G.
Coated Fabrics— Pigments— Lacquers and Varnishes

FDX 813* (PB 82,057; Microfilm X16).

Among a number of miscellaneous reports written in 1941, the following appear—

Plastopal AW in Waxed Fabrics
Softeners for Fabrics coated with Cellulose Nitrate
Use of Polyacrylic Products in modifying Pigments
Polymers for Varnished Textiles

and several on various aspects of lacquer and varnish manufacture, including four reports on the use of super-polyamides in lacquers. C. O. C.

Survey of the Coated Fabrics Industry in Germany
Machinery, Techniques, and Material

FD 107/50* (PB 2,335).

Microfilm copy of a 53 pp. report (in English) prepared by Allied investigators. Four types of fabric are dealt with— (1) Coated with cellulose nitrate, (2) Oil-coated, (3) Coated with plasticised polyvinyl chloride, and (4) Miscellaneous Coatings. There are five appendices, dealing with— (1) Plasticisers and their properties, (2) evaluation of plasticisers for vinyl polymers, (3) fleece-backed coatings, (4) general characteristics of Luvitherm foil, and (5) principal plants visited. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Preparing and Testing various Plastic Compositions
Carbon Blacks— Artificial Leather

FD 516/50* (PB 82,044).

A large number of reports, dealing with plasticisers, polyamides, emulsions, mixed polymers, Igelits and Oppanols, oil-proof paper, rubber dust substitutes, adhesives, etc., include *Testing Soot KG, Ivory Black, and Vine Black as to their Richness and Fastness to Light compared with Lamp Black as Pigments for Synthetic Emulsions* (written in Sept. 1939) and *Artificial Leather from Fibrous Fleecy Material* (Nov. 1939). C. O. C.

I.G. Farbenindustrie A.-G., Oppau
Test for Adipic and Pimelic Acids

Dr. Becke. FD 1473/49*.

Report dated 5th Dec. 1939. When adipic acid is fused with resorcinol and $ZnCl_2$, a dye is produced whose alkaline solution is a deep red. This test allows adipic acid to be detected even in amounts of 0·01% in mixtures of dicarboxylic and higher aliphatic acids. In absence of adipic acid the test serves to detect pimelic acid provided fusion is carried out at 140–150°c. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen
Analytical Methods for Dye Intermediates, Heavy Chemicals, and Solvents

FDX 830* (PB 74,321; Microfilm 27 G).

Microfilm of 243 methods used in 1943 for the analysis of a large variety of dye intermediates and for some heavy chemicals and solvents used in dye manufacture. C. O. C.

Abstracts from British and Foreign Journals and Patents

(The Titles of Patents are abridged and modified)

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Pelleting Dry Flocculent Carbon Black. Phillips Petroleum Co. *B.P.* 638,863.

Obtaining Finely Divided Precipitates. I.C.I. Ltd. *B.P.* 638,564.

Emulsifying or Mixing Apparatus. Nortal Ltd., E. A. Leak, and N. Waring. *B.P.* 637,989.

Container for Pigmented Liquids. P. E. Knudsen, E. H. Heaton, and Pittsburgh Plate Glass Co. *U.S.P.* 2,498,125.

A portable container for heavily pigmented liquids, in which the contents can be readily agitated to obtain uniform dispersion of the pigment after long storage, is described. C. O. C.

Carbon Black. W. B. Wiegand, H. A. Braendle, and Columbian Carbon Co. *U.S.P.* 2,499,437.

Apparatus is described for preparing carbon black from hydrocarbon gas. It is very flexible with respect to the range of its operating conditions and consequently the character of the pigment produced. *U.S.P.* 2,499,438.

The process is modified to produce high yields of uniform quality. C. O. C.

Metallic Powders. Glacier Metal Co. Ltd., W. H. Tait, and P. P. Love. *B.P.* 638,581.

Apparatus in which a jet of molten metal is atomised by a blast of air, superheated steam, or other gas. C. O. C.

Continuous Wet Treatment of Rayon Filaments. H. Crewdson and American Viscose Corpn. *U.S.P.* 2,499,464.

Fibre Pick-up Drum and Squeeze Roll for Loose-fibre Scouring Machine. E. H. Brooks, Snr., E. H. Brooks, Jnr., and E. H. Thompson. *U.S.P.* 2,498,646.

Conditioning Textile Fibres during Production of Yarns. G. H. Thompson. *B.P.* 637,678.

Conditioning of the fibres is obtained by having in their vicinity one or more pipes through which a cooling or refrigerating medium is passed so as to reduce the temperature in the neighbourhood of the pipe. C. O. C.

Processing Thread in Package Form. L. S. Fryer, P. J. E. Andersson, W. J. Jokilehto, and Industrial Rayon Corpn. *U.S.P.* 2,498,540.

Heat-setting. W. G. Helmus and Fair Lawn Finishing Co. *U.S.P.* 2,499,141. *U.S.P.* 2,499,142.

Apparatus is described for the efficient, high-speed heat-setting of textiles containing nylon. C. O. C.

Fabric Dyeing, etc. Machines. J. Dungler. *B.P.* 639,564.

The fabric passes through the machine as an endless band supported on rollers provided at regular intervals. A tank contains the treating liquor through which the fabric passes. As it leaves this tank, the fabric passes through squeeze rollers, and is collected in loose folds in a receiver. On leaving this receiver, the fabric is again extended and supported on other rollers to be fed again into the treating liquor. One of this second set of rollers is adjustably mounted so that it can be moved into a position to allow the ends of the fabric to be sewn together, after which the roller is adjusted so that the run of fabric between the outlet end of the receiver and the treating liquor is extended in readiness for the working of the machine, devices situated in the same run uncurling and guiding the selvedges before the fabric re-enters the liquor. C. O. C.

Drying Cylinders heated with Hot Water. Papierfabrik Balsthal A.-G. *B.P.* 639,007.

Coupling for Drying Cylinder, especially one Using Hot Water as the Heating Medium. Papierfabrik Balsthal A.-G. *B.P.* 638,078.

Fabric-drying Machine. J. Dungler. *B.P.* 639,263.

A machine which allows free shrinkage in both warp and weft effects rapid and even drying over a limited travel. Drying is effected by blowing hot air in jets or sheets over the entire width of the fabric. Preferably the nozzles for the hot air are placed above and below the material, so that it passes between pairs of opposed jets of hot air. C. O. C.

Skewing a Calender Roll. Dunlop Rubber Co. Ltd. and H. Willshaw. *B.P.* 638,290.

Each of the bearings for at least one of the rolls of a calender is kept in an opening in the calender frame by a parallel-sided member on one side and a tapered wedge diametrically opposite. This enables the axis of the roll to be skewed relatively to the axis of the adjacent roll in a direction at right angles to the direction of thrust between the two rolls. C. O. C.

Conveyor Belts for Screen Printing Machines. C. B. Projections (Engineering) Ltd. and C. S. Bell. *B.P.* 639,512.

The material to be printed is conveyed to and from the printing positions on an endless belt having two or more flexible endless steel bands with several narrow rigid transverse elements attached to them, and an outer covering of resilient sheet material bonded to the transverse elements. C. O. C.

Steaming or Ageing. C. L. Wall. *B.P.* 638,402.

The chamber is almost completely exhausted of air, and a continuous or intermittent pressure gradient is maintained throughout the material under treatment. This prevents pockets of gas or superheated steam from developing and causing uneven ageing. C. O. C.

Web Coating. New York & Pennsylvania Co. Inc. *B.P.* 637,717.

A web-coating machine comprises a coating applicator, designed to deposit a film of coating material on the face of a travelling web, means for ejecting gas in jets adjacent to the coated face at velocities sufficiently high to pick up gas from the surrounding atmosphere, and guide means deflecting and flattening the jets for forming a gas brush acting on the deposited coating material. A breast roll receives the coated web and passes it up to a drier, forming an inclined run of web, on which the gas brush acts as it travels round the breast roll. The air tube is adjustable, and baffles are provided to return the excess coating material to the applicator, which consists of a coating pan and a fountain roll, both of which are adjustable relative to the breast roll. Means for humidifying the gas are provided, together with guide rolls carried by the side frames of the applicator. A pair of coating machines may run in tandem, each fitted with a large-diameter drying drum, so that both sides of the web may be coated in one operation. S. V. S.

Automatic Clips for Tenters. J. Dungler. *B.P.* 639,398.

Cemented Pile Fabric. P. S. Smith and C. H. Masland & Sons Inc. *U.S.P.* 2,497,330.

Weatherproofing Textile Fabric Articles. A. D. V. Harnett. *U.S.P.* 2,499,748.

A machine for the wax, etc. proofing of garments and the like. C. O. C.

Garment Presses. Cherry Tree Machine Co. Ltd. and G. Dowell. *B.P.* 639,001.

Screen Printing of Boxes, Bottles, etc. Solar Engineering Equipment Co. *B.P.* 638,286.

Removing Silicic Acid from Water. F. Kopecky and F. Vondruska. (II, p. 487.)

Removing Calcium Hydroxide from Water. F. Kopecky and F. Vondruska. (II, p. 487.)

Screen Printing. K. T. Lindahl, C. A. Heintges, J. P. W. Jacobs and Heintges, Jacobs & Co. (IX, p. 498.)

Decatising. W. N. Hadley and Parks & Woolson Machine Co. (X, p. 501.)

II—WATER AND EFFLUENTS

Synthetic Detergents and Sewage Processing. L. Waddams. *Surveyor*, **109**, 39–40 (1950): *Chem. Abs.*, **44**, 4172 (10th May 1950).

Neither Lissapol N nor Teepol affected primary sedimentation, bacterial activity, sludge digestion, or methane production when tested in concentrations such as are encountered in sewage treatment. Cationic detergents, however, are bactericidal. C. O. C.

PATENTS

Anti-foaming Compositions. S. Stevens and I.C.I. Ltd. *B.P.* 638,403.

Addition to boiler waters of a mixture of tannin (30–60 parts by weight), a long-chain ether of ethylene or polyethylene glycol (3–8), sodium carbonate (30–60), and glassy sodium phosphate (5–20) prevents foaming. C. O. C.

Removing Silicic Acid from Water. F. Kopecky and F. Vondruska. *B.P.* 639,408.

Removing Calcium Hydroxide from Water. F. Kopecky and F. Vondruska. *B.P.* 639,460.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Chemistry of the Autoxidation of Drying Oils. W. O. Lundberg. *Official Digest Federation Paint & Varnish Production Clubs.* No. **302**, 199–211 (1950): *Chem. Abs.*, **44**, 4692 (25th May 1950).

A review with 43 references. C. O. C.

Silicones. H. W. Kohlschütter. *Fortschr. chem. Forsch.*, **1**, 1–60 (1949): *Chem. Abs.*, **44**, 4714 (25th May 1950).

A review of the chemistry of silicones giving 147 references. C. O. C.

Use of Oils in Wool Processing—Quantities and Costs in Bygone Days. G. V. Carrette. *Wool Record*, **77**, 1899, 1923 (22nd June 1950).

Historical, covering the period from the 12th century to the present day. C. O. C.

PATENTS

Conditioning Acetate Rayon Yarns. C. F. Chandler and Du Pont. *U.S.P.* 2,497,536.

Addition of a small amount of polyvinyl alcohol to aqueous oil emulsions used for finishing or lubricating acetate rayon yarns gives marked improvement in quality and handle and imparts to the yarn a lower coefficient of friction. C. O. C.

Textile Lubricants. J. R. Caldwell and Eastman Kodak Co. *U.S.P.* 2,496,776.

Compounds of formula—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_2H_4{\cdot}NH{\cdot}CO{\cdot}R$$

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NH{\cdot}CO{\cdot}R$$

or $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}N(C_2H_4{\cdot}NH{\cdot}CO{\cdot}R)_2$

(R = Alk of 8–24 C) are useful lubricants and softeners for textiles. They are also useful as plasticisers for cellulose esters and ethers and for vinyl resins. They may also be used as emulsifiers, detergents, and surface-active agents. C. O. C.

Self-scouring Lubricant for Wool. H. F. Leupold, M. J. Kelley, and Nopco Chemical Co. *U.S.P.* 2,496,631.

A mixture of a non-resinifying oil, a liquid monoacylated organic fatty ester, and, as an emulsifying agent, the condensate obtained by heating one equivalent weight of a fatty acylating substance having an acyl chain of > 7 C with 1·5–4·0 mol. of diethanolamine, ethylmonoethanolamine, di*iso*propanolamine, or 2-amino-2-methyl-1-propanol acts as a lubricant in wool carding and spinning and as a scouring and milling agent in subsequent wet processing. C. O. C.

Antistatic Agents. A. L. Fox and General Aniline & Film Corpn. *U.S.P.* 2,498,408.

Lauryl ethyl hydrogen orthophosphate is an excellent antistatic agent for application to textiles, e.g. by adding 1–10% to the lubricant used or by adding it to the acetone solution of cellulose acetate used to make acetate rayon. C. O. C.

Wetting, Detergent, Dispersing, and Levelling Agents. M. De. Groote, B. Keiser, and Petrolite Corpn. Ltd. *U.S.P.* 2,499,360.

Compounds of formula—

$$R^5{\cdot}[O{\cdot}R^2]_n{\cdot}O{\cdot}R^4(R^3){\cdot}CH(R^1){\cdot}R^4(R^3){\cdot}O{\cdot}[R^2{\cdot}O]_n{\cdot}R^5$$

(R^1 = H or an organic radical of < 8 C; R^2 = alkylene or hydroxyalkylene of < 5 C; R^3 = hydrocarbon of 1–24 C *para* to the O in R^4; R^4 = monocyclic nucleus derived from a phenol in which the O is *ortho* to the C of the formula; R^5 = H or an acyl radical of a monocarboxylic acid of < 33 C (if either R^5 = acyl, then at least one must be of 8–32 C); n = 1–60) are used. *U.S.P.* 2,499,361.

Similar compounds in which $R^3 = CH_3$ are used. *U.S.P.* 2,499,362.

Similar compounds in which R^3 = hydrocarbon of 2–3 C are used. *U.S.P.* 2,499,363.

Similar compounds in which R^3 = hydrocarbon of 4–8 C are used. *U.S.P.* 2,499,364.

Similar compounds in which R^3 = hydrocarbon of 9–24 C are used. C. O. C.

Soap-containing Compositions resistant to Hard Water. Procter & Gamble Co. and W. C. Preston. *B.P.* 638,637.

Carboxyamides used with soap alone do not inhibit curd formation in hard water, but when used with soap and a sulphated or sulphonated detergent, they have a marked power of inhibiting lime soap precipitation and curd formation. C. O. C.

Aqueous Solutions of Soapless Detergents. F. J. Pollok and I.C.I. Ltd. *B.P.* 639,173.

Aqueous solutions of soapless detergents are given increased viscosity, resulting in less waste during use, by incorporating an alkali-metal salt of an acid ester of a partly esterified polyvinyl alcohol in which the vinyl alcohol groups are partly acetylated, partly esterified by a polybasic acid, and partly unreplaced, e.g. a polyvinyl acetate-maleate. J. W. B.

Antioxidants. H. B. Kellog. *U.S.P.* 2,497,061.

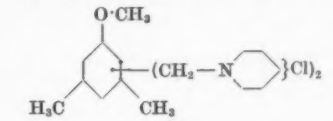
Compounds of formula HO·N:CAlk·CHAlk·CAlk:N·OH, e.g. 3-methyl-2:4-pentanedione dioxime, are very efficacious antioxidants compatible with a wide variety of substances and not staining rubber on exposure to light. C. O. C.

Conditioning Starch for Enzymic Conversion. J. M. Newton, L. D. Ough, and Clinton Industries Inc. *U.S.P.* 2,497,838.

Addition of phytic acid or Ca or Mg phytate to starch slurry overcomes the inhibiting action on enzyme conversion exerted by any Cu or heavy metals present. C. O. C.

Quaternated 3:5-Dimethylphenyl Ethers. P. L. de Benneville, L. J. Armstrong, L. H. Bock, and Röhm & Haas Co. *U.S.P.* 2,499,213.

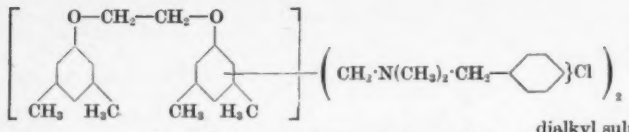
3:5-Dimethylphenyl ethers having quaternary methyleneammonium groups as phenyl substituents, e.g.—



readily react with cellulose to form cellulose ethers. C. O. C.

Quaternary Ammonium Compounds from Halogenomethylated Bis-3:5-dimethylphenyl Diethers. P. L. de Benneville, L. H. Bock, and Röhm & Haas Co. *U.S.P.* 2,499,214.

Bis-3:5-dimethylphenyl diethers (in which the two O atoms are separated by 2 or 3 C) having quaternary ammonium groups joined to the phenyl ring through methylene linkages, e.g.—



readily react with cellulose to form cellulose ethers. They are obtained by treating the corresponding -halogenomethyl compounds with amines. C. O. C.

Quaternary Ammonium Derivatives from Halogenomethylated Polymers of 3:5-Dimethylphenyl Ethers. P. L. de Benneville, L. H. Bock, and Röhm & Haas Co. *U.S.P.* 2,499,215.

Polymeric quaternary ammonium compounds which serve as cationic soaps when they contain a long-chain substituent and as modifying agents for cellulose contain 3:5-dimethylphenoxy nuclei joined through methylene bridges. There are at least sufficient quaternary methyleneammonium groups present to render the compounds water-dispersible. They are obtained by treating an ether of 3:5-xylenol with formaldehyde in presence of an acid catalyst, then treating the resulting soluble resin with formaldehyde and excess hydrohalide, and finally treating the halogenomethylated material with a tertiary amine. An example is the quaternary salt from benzyldimethylamine and chloromethylated 3:5-dimethylanisole–formaldehyde polymer. Cellulosic materials impregnated with these compounds and heated at 200–350°F. are rendered water-repellent and dimensionally stable, and their handle and dyeing properties are altered. C. O. C.

Insolubilised Cellulose Ethers useful as Textile Finishes or for Casting. A. L. Houk, L. H. Bock, and Röhm & Haas Co. *U.S.P.* 2,498,208.

Cellulose is treated with an alkali hydroxide to form alkali cellulose, which is then treated with *iso*butylene oxide to yield an alkali-soluble product. This is then dissolved in aqueous alkali. This solution is then used for coating or impregnating, e.g. textiles, or is cast on a foil. It is then neutralised, treated with a soluble cobalt salt, and heated to insolubilise the cellulosic material. C. O. C.

Ether Derivatives—Auxiliary Agents. M. Katzman, A. K. Epstein, and Emulsol Corpn. *U.S.P.* 2,496,875.

Ethers of alcoholamines in which the radical which unites with the alcoholamine to produce the ether is a derivative of an aliphatic polyhydroxy substance in which at least one hydroxyl H is replaced by an organic radical of > 5 C and in which another hydroxyl H is replaced by an aliphatic acyl radical of < 6 C, e.g.—

$C_{12}H_{25}\cdot O\cdot C_2H_4\cdot O\cdot C_2H_4\cdot O\cdot CO\cdot CH_2\cdot O\cdot C_2H_4\cdot N(C_2H_4OH)_2$

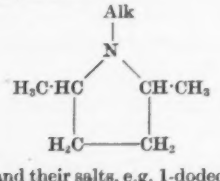
are surface-active agents of unusual resistance to acids and alkalis. They have a wide range of uses as detergents and auxiliary agents for textiles, leather, etc. C. O. C.

Copolymers of *N*-Vinyllactams and Polymerisable Resins. J. H. Werntz and Du Pont. *U.S.P.* 2,497,705.

The water-soluble products of the copolymerisation of not < 5 mol. of an *N*-vinyllactam with 1 mol. of an ester of a monocarboxylic acid containing > 7 C are highly effective as either non-ionic or cationic surface-active agents. Thus in neutral or mildly alkaline solution they are detergents, while in acid solution they are softening agents and dyeing assistants for cellulosic materials. C. O. C.

1-Alkyl-2:5-dimethylpyrrolidines. A. W. Ralston, J. Harwood, and Armour & Co. *U.S.P.* 2,497,839.

Compounds of formula—



(Alk of > 11 C) and their salts, e.g. 1-dodecyl-2:5-dimethylpyrrolidine, are surface-active agents useful for many purposes. C. O. C.

Improving the Fastness to Water of Water-soluble Dyes. Sun Chemical Corpn. *B.P.* 638,323.

The products obtained by treating an aliphatic amine containing 12–18 C first with formaldehyde and then with a dialkyl sulphate containing 2–4 C are useful for improving the fastness to water of direct cotton dyes on cellulose. C. O. C.

Aqueous Dispersions of Ethylene Polymers containing a Salt of a Polymeric Amic Acid. M. E. Cupery and Du Pont. *U.S.P.* 2,496,989.

The water-soluble basic amine salts of an *N*-monoalkyl-substituted polymeric amic acid of an interpolymer of a polymerisable organic compound containing an ethylenic double bond as the sole aliphatic carbon–carbon unsaturation with a butenedioic anhydride (the recurring two non-keto carbonyl groups in the polymeric amic acid being attached directly to adjacent carbon atoms of the polymeric chain which contains groups in which the amide N atom carries H and a long-chain monoalkyl radical of > 6 C) are dispersing agents which yield stable aqueous dispersions of ethylene polymers. Such dispersions are useful for coating paper, cloth, etc. C. O. C.

Fixing Insoluble Substances on Fibres. British Rubber Producers' Research Assocn. and C. M. Blow. *B.P.* 638,090.

Insoluble substances can be fixed on fibres by treating the latter with a mixture of an aqueous dispersion of the insoluble substance and an aqueous dispersion of rubber, both dispersions being positively charged and prepared with the aid of a cationic soap. C. O. C.

Resinous Aromatic Acid Salts of a Guanidine as Mothproofing Agents. V. Migrdichian and American Cyanamid Co. *U.S.P.* 2,499,226.

The salts produced by treating free guanidine or a substituted guanidine with aromatic acids have a resinous character. They are soluble in organic solvents, and such solutions are used for mothproofing, e.g. a 3% solution of guanidine benzoate or dixylylguanidine benzoate in a mixture of ethyl alcohol and carbon tetrachloride. Unlike the fatty acid salts hitherto used, e.g. dixylylguanidine oleate, they do not impart a greasy handle to the mothproofed material. C. O. C.

Compositions containing Cerium Acetate—Spotproofing Agents for Rayon Hose, Components for Paints, etc. C. E. Griffin. *U.S.P.* 2,497,546.

An aqueous–*iso*propanolic suspension of 5–25 parts by weight of cerium acetate and 5–25 parts of an alcohol-soluble resin has wide uses, e.g. for spotproofing rayon hose, incorporation in paints to render them applicable to wet or damp surfaces, etc. C. O. C.

Flame-resistant Finish for Cellulosic Materials. American Cyanamid Co. *B.P.* 638,434.

Salts of an aminotriazine with pyrophosphoric acid, e.g. melamine pyrophosphate, are excellent flameproofing agents for cellulosic materials. They are insoluble in water, and may be formed on the material or applied from aqueous dispersion. They are preferably used in admixture with hexamethylenetetramine to reduce any loss in strength of the treated material and/or a resinous binding agent to prevent them from crystallising and dusting off the proofed material. C. O. C.

Interpolymers of Fumaric Esters and a Chlorinated Alkene—Flameproofing Agents. J. G. Kuderna, Jr., R. H. Snyder, and United States Rubber Co. *U.S.P.* 2,498,084.

Interpolymers of an allylic fumarate and not $< 10\%$ of a compound of formula $C_nH_{2n-x}Cl_x$ ($n > 2$, $x = 1$ or 2), obtained by heating the monomers together below 120°C. in presence of a peroxide, are infusible solids useful as flameproofing agents. C. O. C.

Interpolymers of Styrene, Fumaric Esters, and Chlorinated Alkenes. P. O. Tawney, J. G. Kuderna, Jr., and United States Rubber Co. *U.S.P.* 2,498,099.

Heating a mixture of not $> 40\%$ by weight of a fumarate, not $< 10\%$ on the weight of the fumarate of a compound of formula $C_nH_{2n-x}Cl_x$ ($n > 2$, $x = 1$ or 2), and styrene at 25–120°C. in presence of a peroxide catalyst yields ternary interpolymers useful in coating and water- and/or flame-proofing compositions. C. O. C.

Ethylene Polymer Emulsions. L. Seed and I.C.I. Ltd. *B.P.* 639,025.

Aqueous emulsions of solid ethylene polymers are prepared by polymerising ethylene, alone or with interpolymerising constituents, at > 50°C. and > 200 atm., in presence of water, a non-ionic emulsifying agent, and an organic sulphonic acid or derivative. In one example the *iso*octylphenyl ether of a polyethylene glycol containing 20–30 C (5·4 parts by wt.), sodium oleo-*p*-anisididesulphonate (16), a 5% benzene soln. of di-*tert.*-butyl peroxide (6·2), and ethylene (456) are added to water (1000). Reaction proceeds at 180°C. and 1300 atm., with addition of ethylene to maintain the pressure. The product is a mobile aqueous emulsion containing 10% by wt. of solid polymer, and is useful for coating textiles with flexible films and as a textile adhesive. J. W. B.

Stable Aqueous Dispersions of Resins by using Ammonium Alginate. W. C. Mast and U.S. Secretary of Agriculture. *U.S.P.* 2,498,694.

Stable aqueous dispersions, suitable for brushing, spraying, dipping, or calendering, and readily pigmented, are obtained by heating methyl acrylate in aqueous medium in presence of a synthetic ionic surface-active wetting and emulsifying agent, a peroxide catalyst, ammonia, and ammonium alginate. C. O. C.

Alkali-metal Pentaoctyl Tripolyphosphates— Stabilisers for Vinyl Resins. C. E. Huff, G. A. Zimmerman, and United States Rubber Co. *U.S.P.* 2,499,503.

Compounds of formula $(C_8H_{17})_5M_5(P_3O_{10})_2$ (M = alkali metal) are used. In the case of fabric coatings the stabiliser is added directly to the organic solution of the vinyl resin. C. O. C.

Resinous Fungicidal Compositions. H. A. Bruson and Röhm & Haas Co. *U.S.P.* 2,497,927.

The copolymers of equimolecular amounts of maleic or chloromaleic anhydride and an ether of formula $R^1(O{\cdot}CH_2{\cdot}CR^2{:}CH_2)_n$ (R^1 = chlorinated Ar containing 1–5 Cl; R^2 = H or CH_3; n = 1 or 2) are mildewproofing agents for textiles, leather, paper, etc. C. O. C.

Dialkylsilylene Derivatives of Ricinoleic Esters— Plasticisers for Cellulose Nitrate. R. E. Christ and U.S. Industrial Chemicals Inc. *U.S.P.* 2,496,335.

Compounds of formula—

$$Alk^1{}_2Si(O{\cdot}CH(C_6H_{13}){\cdot}CH_2{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}COOAlk^2)_2$$

(Alk^1 and Alk^2 of 1–6 C) are plasticisers which impart to cellulose nitrate an increased useful working temperature range and increased flexibility at low temperatures. C. O. C.

Trialkylsilyl Derivatives of Ricinoleic Esters— Plasticisers for Cellulose Nitrate. K. A. Earhart and U.S. Industrial Chemicals Inc. *U.S.P.* 2,496,340.

Compounds of formula—

$$Alk^1{}_3Si{\cdot}O{\cdot}CH(C_6H_{13}){\cdot}CH_2{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}COOAlk^2$$

(Alk^1 and Alk^2 of 1–8 C) when combined with cellulose nitrate yield films of high folding flexibility and low elastic modulus. C. O. C.

Emulsifying Agent. T. Robinson, C. H. Bascom, and Lancaster Processes Inc. *U.S.P.* 2,499,002.

An emulsifying agent yielding emulsions of liquefiable materials which on drying can no longer be dispersed in water is obtained by adding an alkaline aqueous dispersion of clay to a boiling solution of an aluminium salt in presence of sufficient alkali to precipitate the aluminium as a hydrated gelatinous precipitate. C. O. C.

Solvents for Polyacrylonitrile. R. Hill, R. G. A. New, S. M. Todd, and I.C.I. Ltd. (VI, p. 496.)

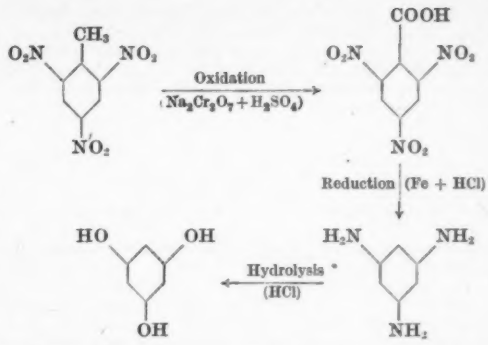
Whitening Agents for Paper. H. G. Cook, V. G. Morgan, and I.C.I. Ltd. (XI, p. 501.)

Aqueous Dispersions of Reaction Products of High Molecular Weight from Dihalogenohydrocarbons and Polysulphides. N.V. De Bataafsche Petroleum Maatschappij. (XIII, p. 503.)

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

TNT into Phloroglucinol. M. L. Kastens and J. F. Kaplan. *Ind. Eng. Chem.*, **42**, 402–413 (March 1950).

A full description is given of the large-scale process for the manufacture of phloroglucinol by the reactions—



including processing conditions, constructional materials used, safety procedures, power consumption, effluent disposal, etc. Phloroglucinol is used chiefly as a developer in photocopying, but it is also of value as a developer for diazotised black dyes, particularly on acetate rayon in replacement of 2:3-hydroxynaphthoic acid. Possible future uses for phloroglucinol are discussed, and the properties of some phloroglucinol derivatives are tabulated. W. K. R.

Structure of the Diazonium Ion. P. F. Holt and B. I. Bullock. *Nature*, **165**, 817 (20th May 1950).

According to the accepted constitution of the diazonium ion, resonance should exist between the two forms—

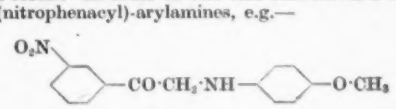
Starting with phthalimide containing radioactively labelled nitrogen, aniline was synthesised, diazotised, and coupled with β-naphthol, and the product was split by reduction to aniline and α-amino-β-naphthol. If the above resonance exists, the labelled nitrogen should be equally divided between these two, but if not, labelled nitrogen should be entirely in the aniline. In fact, > 97% of the labelled nitrogen remains in the aniline, indicating that the resonance does not exist. A. S. F.

***Cis-Trans* Isomerisation of Azobenzene in Solution.** J. Halpern, G. W. Brady, and C. A. Winkler. *Canadian J. Res.*, **B 28**, 140–155 (April 1950).

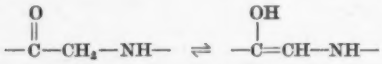
The kinetics of the *cis–trans* isomerisation of azobenzene has been studied in 16 pure solvents, and a linear relation between activation energy and square root of internal pressure of solvent was found, in agreement with the theory of this unimolecular, non-ionic reaction derived from existing theories of solutions and chemical kinetics. The kinetics of the reaction in mixed solvents indicates that the azobenzene is preferentially surrounded by the component in which it is more readily soluble. A. S. F.

Separated Chromophoric Systems. XXVI— Colour Phenomena in Nitrophenacyl Derivatives of Aromatic Amines. E. A. Smirnov. *J. Gen. Chem.* (*U.S.S.R.*), **20**, 696–707 (April 1950).

The compounds examined in this series of papers contain two conjugated chromophoric systems, one containing an electron-accepting group such as NO_2, and the other an electron-donating group such as NH_2 or OH. These systems are separated by a group, such as –CO·NH– or $–CH_2{\cdot}CO{\cdot}NH–$, which breaks the conjugation. The colour phenomena found in these compounds are explained on the supposition that the two systems can interact through their external fields. Consideration is now given to the effect of interposing CH_2 between CO and NH in the connecting group. It is considered that the consequent reduction in the interaction between CO and NH will enable these groups to play fuller parts in the chromophoric systems to which they belong, and a deepening of colour should result. In order to test this contention a number of *N*-(nitrophenacyl)-arylamines, e.g.—



are compared with the corresponding nitrobenzoylarylamines. In all cases the former are considerably deeper in colour (e.g., in the example cited, red–orange instead of pale yellow). The interposition of $C(CH_3)_2$ in place of CH_2 leads to a similar bathochromic effect, and the possibility of the tautomerism—



playing a considerable part is therefore ruled out.

A. E. S.

Absorption Spectra of some Intermediates and Azo Dyes of the Naphthalene Group. V. V. Perekalin and M. V. Savostyanova. *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **12**, 585–594 (1948): *Chem. Abs.*, **44**, 4330 (25th May 1950).

The absorption spectra of the following dyes—4-phenylazo-1-naphthylamine; 2- and 4-phenylazo-1-naphthol; 2-, 6-, and 8-phenylazo-1:5-aminonaphthol; 2- and 6-phenylazo-1:5-aminonaphthol-4-sulphonic acid; 2- and 8-phenylazo-1:5-aminonaphthol-6-sulphonic acid; 2:8-bisphenylazo-1:5-aminonaphthol-6-sulphonic acid— and of 12 intermediates were measured with a Beckman spectrophotometer. All showed the short-wave maxima of the naphthalene molecule. One short-wave maximum was constant, another shifted as a function of substituents. There was a "main" maximum in the visible spectrum varying according to the substituents. The position of this maximum is independent of pH in *o*-hydroxy compounds. This "main" maximum is not characteristic of the azo group but is due to interaction of the azo group with the naphthalene nucleus and side groups. In the above azo dyes a hydrogen bond may exist. C. O. C.

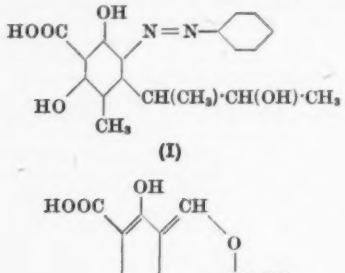
Reversible Polymerisation and Molecular Aggregation of Dyes. L. Michaelis. *J. Phys. Colloid Chem.*, **54**, 1–17 (1950): *J. Textile Inst.*, **41**, A 254 (May 1950).

A review of reversible polymerisations in the field of "molecular compounds" is presented, in the following sections— (*a*) The reversible molecular aggregation of dyes; changes which occur in the spectra of some dyes with change of solvent (e.g. from aqueous to alcoholic media) are described and discussed. (*b*) Quinhydrone-like molecular compounds; quinhydrones formed from a quinol and a quinone and the analogous compounds formed from an aromatic *p*-diamine and a corresponding diimine are considered. (*c*) Molecular compounds composed of two different molecular species, e.g. the compounds of phenol and quinone or chloranil and hexamethylbenzene.

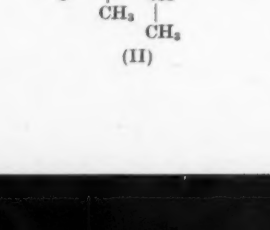
C. J. W. H.

Citrinin—I. T. S. Gore, T. B. Panse, and K. Venkataraman. *Proc. Indian Acad. Sci.*, **29 A**, 289–308 (1949): *Chem. Abs.*, **44**, 3980 (10th May 1950).

Comparison of the azo dyes from citrinin and its H_2SO_4 hydrolysis product with those of 2- and 4-phenylazoresorcinol derivatives indicates that the azocarboxylic acid from citrinin and $C_6H_5N_2Cl$ has the formula (I). Study of the reactions of citrinin with diazonium salts and of their absorption spectra confirm Robertson's suggestion that the formula for citrinin is (II).



(I)



(II)

C. O. C.

New Procedures in Synthesis of 2-Hydroxy-1:4-naphthaquinone. D. Molho and C. Mentzer. *Experientia*, **6**, 11, 12 (1950): *Chem. Abs.*, **44**, 4455 (25th May 1950).

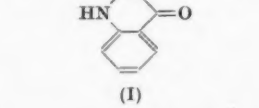
2-Methoxynaphthalene was oxidised with CrO_3 or lead tetraacetate in acetic acid to 2-methoxy-1:4-naphthaquinone, which was demethylated to yield lawsone. The yield was very low. A more practical preparation involves the action of H_2O_2 on *a*-naphthol in alkaline aqueous solution, the sodium salt of lawsone being precipitated in a pure condition. C. O. C.

Radioactive Oxazine Dye. H. A. Sloviter. *Science*, **110**, 687–688 (1949): *Chem. Abs.*, **44**, 4005 (10th May 1950).

Diazotised *p*-toluidine with $H^{131}I$ gave $p\text{-}^{131}I\cdot C_6H_4\cdot CH_3$, which with Br formed $p\text{-}^{131}I\cdot C_6H_4\cdot CH_2Br$. Addition of *a*-naphthylamine gave $a\text{-}p\text{-}^{131}I\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_{10}H_7$, which was converted to the ^{131}I derivative of 5-*p*-iodobenzylamino-9-diethylaminobenzo[*a*]phenoxazine (cf. *C.I.* 914) on refluxing with 5:2-nitrosodiethylaminophenol. Of the 18·5 millicuries of ^{131}I used, 4·2 millicuries were obtained in the 8 g. of product. C. O. C.

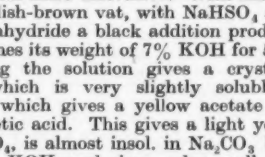
Anil Red. P. Seidel. *Chem. Ber.*, **83**, 26–28 (1950): *Chem. Abs.*, **44**, 5102 (10th June 1950).

When 40 g. indigo white 20% paste is heated for 8 hr. at 180°c. with 50 c.c. 5% $Na_2S_2O_4$ and 3 c.c. 35% NaOH, and the cold mixture treated with air and acidified, 2·3 g. *ana*-quinindolinecarboxylic acid is obtained as well as 4 g. of a dark residue which is extracted with 1% acetic acid. Fractional neutralisation of the acid solution yields 0·8 g. anil red (I). This dissolves in conc. H_2SO_4 to a

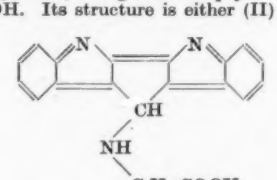


(I)

brown–black solution, in dil. acetic acid to blue–red, and in alcoholic alkali to a deep grass-green. On adding HNO_3 or HCl to its solution in acetic acid, brown–black crystals separate. Warming I with conc. HNO_3 gives a black crystalline nitro derivative. With alkaline $Na_2S_2O_4$ I gives a reddish-brown vat, with $NaHSO_4$ a yellow, and with acetic anhydride a black addition product. Heating I with five times its weight of 7% KOH for 5 hr. at 120°c. and acidifying the solution gives a crystalline yellow compound, which is very slightly soluble in organic solvents and which gives a yellow acetate when heated with 60% acetic acid. This gives a light yellow solution in conc. H_2SO_4, is almost insol. in Na_2CO_3 but more sol. in warm 10% KOH, and gives a deep yellow liquid with alcoholic KOH. Its structure is either (II) or (III).



(II)



(III)

C. O. C.

Azo Dyes derived from 4-Hydroxyquinaldine—I. A. Meyer and L. Silberstein. *Bull. Soc. chim. France*, 590–593 (1948): *Chem. Abs.*, **44**, 4255 (10th May 1950).

Diazotised amines couple in strongly alkaline solution, entering the 3-position. With benzidine a temperature of 40–50°C. is necessary to obtain the disazo compound. The monoazo derivatives from diazotised sulphanilic acid, amino-G acid, and naphthionic acid give poor dyeings on wool; that from amino-R acid, however, is a clear scarlet. Dyeing in all cases is slow, and the dyeings cannot be chromed. Disazo and polyazo dyes may be obtained from diazotised benzidine, tolidine, and dianisidine coupled with hydroxyquinaldine, H acid, naphthoic acid, Nevile and Winther's acid, γ acid, J acid and salicylic acid, amino-H acid, amino-J acid, and amino-γ acid. Benzidine was also coupled with G acid. All the products are direct cotton dyes, but in general the presence of the quinaldine nucleus results in weaker and duller colours than would be obtained by using other intermediates. C. O. C.

Relationship between the Planar Structure of Polymethin Dyes and their Absorption Properties. P. Bruylants, A. van Dormael, and J. Nys. *Bull. Classe sci., Acad. roy. Belg.*, **34**, 703–715 (1948): *Chem. Abs.*, **44**, 3819 (10th May 1950).

Scale drawings of thiacarbocyanines show that planar structure is impossible in certain cases because of steric hindrance. The part of the molecule outside the plane takes no part in the mesomerism and has no influence other than by induction. The fragment which forms the principal resonance chain responsible for absorption can be determined from the respective values of the various carriers of electric charge and the absorption maxima of related compounds. C. O. C.

Brown Pigment of Orthoptera. S. Okay. *Commun. Faculté Sci. Univ. Ankara*, **1**, 178–186 (1948): *Chem. Abs.*, **44**, 4151 (10th May 1950).

The brown colour of brown varieties of several Orthoptera is probably due to an ommochrome pigment. Reasons are adduced for including acridioxanthin among that class of pigments. C. O. C.

Flake Metal Powders—Application, Manufacture, and Testing. H. Meyersberg. *Symposium on Powder Metallurgy, Iron & Steel Inst.* (London), *Special Rept.* No. **38**, 37–46 (1947): *Chem. Abs.*, **44**, 4389 (25th May 1950).

The flaky or lamelliform type of metal powder contrasts sharply with other shapes. Flaky powders have high covering power and low apparent density compared with atomised and granular products. Flaky powders can be made by two methods—(*a*) in stamps, and (*b*) in a ball mill modified to extra hammering action. These methods are described in detail. Flaky powders have wide application in paints because of their covering and leafing powers and lustre. Test methods for covering power, leafing power, fatty acid content, particle size distribution, combustion properties, and hydrogen evolution are given. C. O. C.

Ferrous and Non-ferrous Metal Powders. G. L. Miller. *Symposium on Powder Metallurgy, Iron & Steel Inst.* (London), *Special Rept.* No. **38**, 8–14 (1947): *Chem. Abs.*, **44**, 4390 (25th May 1950).

The processes for producing metal powders are classified as follows—(1) milling, (2) machining, (3) atomising, (4) granulation or shotting, (5) graining, (6) reduction of metallic oxides, (7) reduction of metallic salts, (8) electrolysis, (9) carbonyl process, (10) hydride process, and (11) miscellaneous. The applications of the various methods are reviewed, and characteristics of the powders produced are briefly discussed. C. O. C.

Ochre—Formation, Deposits, and Future. V. Charrin. *Ind. céram.* (Ed. B. *Rev. Matériaux Construction*) No. **386**, 108, 110 (1948): *Chem. Abs.*, **44**, 5069 (10th June 1950).

Clays containing > 20% Fe_2O_3 are called ochres. Yellow ochre is coloured by hydrated iron oxide. Typical analyses show—Fe_2O_3 20–40, clay (Al silicate) 50–70, and H_2O 3–10% (limonite of Béhobie is a true ochre containing Fe_2O_3 39% and clay 48%). French deposits at Vaucluse, 12 m. thick, are derived from glauconite in the Middle Cretaceous. The ore is blunged, washed free from sand, settled, dried in the open, milled, bolted, and blended or calcined as required. Over 80 varieties of hue are produced. C. O. C.

Ultramarines. J. S. Prener and R. Ward. *J. Amer. Chem. Soc.*, **72**, 2780–2781 (June 1950).

A mixture of $3Na_2CO_3 + 3Al_2O_3 + 6SiO_2 + Na_2S$ was heated in nitrogen for 15 hr. at 900°C. The pale-coloured product was quite stable when ignited in air. Heated in a stream of H_2S for 2 hr. at 900°C., a yellow–green product resulted which when ignited in air yielded deep blue ultramarine. Substitution of 2NaCl for Na_2S in the primary mixture resulted in production of sodalite, which on heating in H_2S and air ignition as above yielded ultramarine, all the Cl having been replaced by S. Heating sodalite in a stream of H_2 and Se vapour at 1000°C. followed by air ignition yielded a red–brown product, which X-ray examination showed to have the structure of ultramarine. C. O. C.

PATENTS

Cyclic Aminobenzaldehyde Acetals of 1:2- and 1:3-Glycols. Du Pont. *B.P.* 638,895.

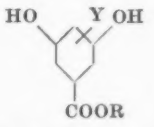
Cyclic aminobenzaldehyde acetals of 1:2- and 1:3-glycols, the glycol residues containing 2–4 C, are obtained by reducing the corresponding cyclic acetals of nitrobenzaldehydes. They are used *inter alia* in preparing polyvinylacetal colour formers. C. O. C.

***N*-Acyl-*N*-Arylhydrazines—Developers for Azo Dye Images.** W. E. Hanford and General Aniline & Film Corpn. *U.S.P.* 2,498,418.

4-Bromoresorcinol as Coupling Component in Diazotype Printing. General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. *B.P.* 638,419.

Colour Couplers for Diazotype Printing. General Aniline & Film Corpn. and J. M. Straley. *B.P.* 638,163.

Compounds of formula—



(R = aliphatic or araliphatic; Y = H, Alk, or Hal) are used. C. O. C.

Solid Diazo Complexes. J. M. Straley and General Aniline & Film Corpn. *U.S.P.* 2,498,722.

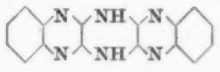
Solid diazo complexes can be produced by adding sulphonated resinous compounds to the diazotisation solution. They are soluble in water and hydrophilic organic solvents, and may be used for any azo dye process where separation from the diazotisation solution and stability to decomposition of the diazo compound are desirable, e.g. in diazotype layers. C. O. C.

Tetrahydroanthraquinones. L. H. Dawsey, R. R. Umhoefer, C. K. Muehlhausser, and Buffalo Electro-Chemical Co. Inc. *U.S.P.* 2,495,229.

Tetrahydroanthraquinones, useful in making hydrogen peroxide, are prepared by passing hydrogen into a solution of anthraquinone or a 2-alkylanthraquinone in a solvent, e.g. dioxan, in presence of a porous nickel catalyst at 20–75°C. and 1–3 atm. pressure. R. K. F.

Fluorescent Azine Derivatives. J. L. Switzer and R. A. Ward. *U.S.P.* 2,495,202.

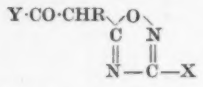
Substances which fluoresce orange to red in aqueous solution are made by converting complex azines of the type—



to the corresponding quaternary ammonium compounds, e.g. by heating with excess methyl *p*-toluenesulphonate. The complex azines are prepared by first condensing an *o*-phenylenediamine with oxalic acid in ethylene glycol to give a 2:3-dihydroxyquinoxaline, which is converted to the corresponding 2:3-dichloro derivative by treating with phosphorus oxychloride and phosphorus pentachloride. The dichloro derivative is finally fused with the corresponding 2:3-diamino derivative (made by treating the *o*-phenylenediamine with cyanogen in methanol). R. K. F.

Colour Couplers. Gevaert Photo-Producten N.V. and P. L. J. R. Merckx. *B.P.* 638,039.

Compounds of formula—



(X and Y = subst. or unsubst. Alk or alkylene, R = H or a substituent which splits off during development) are used as photographic colour couplers for development with a primary aromatic amine. C. O. C.

Phenolic Colour Formers for Cyan Dyes. H. T. Thompson and General Aniline & Film Corpn. *U.S.P.* 2,498,466.

Compounds of general formula—

$$R^1{\cdot}CO{\cdot}NH{\cdot}R^2{\cdot}R^3{\cdot}NH{\cdot}CO{\cdot}R^1$$

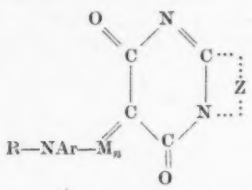
or

$$R^1{\cdot}CO{\cdot}NH{\cdot}R^2{\cdot}NAlk{\cdot}CO{\cdot}R^1$$

(R^1 = a phenolic radical in which the phenolic OH is *ortho* to the amido group; R^2 = arylene; R^3 = alkylene) yield blue–greens when used as photographic colour formers. C. O. C.

Polycyclic Diketopyrimidines. General Aniline & Film Corpn. and A. W. Anish. *B.P.* 638,504.

Compounds of formula—



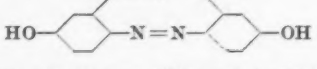
(M = methin; R = H or acyl; Z = atoms to make a nucleus containing two hetero atoms; n = 1 or 3, and the central methin group can be substituted by Cl or Br when n = 3) are intermediates for *mero*cyanine dyes. C. O. C.

Cyanine Dye Intermediates containing an *N*-Aryloxyalkyl, *N*-Arylthioalkyl, or *N*-Arylselenoalkyl Group. A. W. Anish and General Aniline & Film Corpn. *U.S.P.* 2,496,842.

Treating a 5- or 6-membered nitrogenous heterocyclic base having a reactive group in the 2-position to the N atom with an aryloxyalkyl, arylthioalkyl, or arylselenoalkyl *p*-toluenesulphonate yields cyanine dye intermediates which, in turn, produce sensitising dyes of large molecular bulk. C. O. C.

Azo Compounds derived from *m*-Pentadecylphenol. C. R. Dawson, D. Wasserman, and Harvel Corpn. *U.S.P.* 2,496,151.

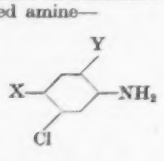
Azo dyes and pigments are made by coupling diazo compounds with hydrogenated cardanol or hydrogenated cashew nut shell liquid (see *U.S.P.* 2,181,119), which consist essentially of *m*-pentadecylphenol. Reduction cleavage of such azo compounds gives *p*-amino-*m*-pentadecylphenol, which may be diazotised and coupled with *m*-pentadecylphenol under alkaline conditions to give the yellow–orange azo dye—



E. S.

Azoic Dyes. W. H. von Glahn and General Aniline & Film Corpn. *U.S.P.* 2,496,255.

Azoic dyes are made in substance or on the fibre by coupling a diazotised amine—



(X and Y = methoxy or ethoxy) with an arylamide of an *o*-hydroxycarboxylic acid having > 2 fused rings. Thus the triazene derived from 5-chloro-2:4-dimethoxyaniline and sarcosine is mixed with the *o*-toluidide of 2:3-hydroxyanthracenecarboxylic acid, printed on cellulose fibres, and developed with acid steam to give bluish blacks. E. S.

Brown and Black Azoic Dyes. W. H. von Glahn and General Aniline & Film Corpn. *U.S.P.* 2,497,246.

Brown and black azoic dyes are made in substance or on the fibre by coupling a diazotised 5-chloro-2:4-dialkoxyaniline with suitable monoazo compounds; e.g. 5-chloro-2:4-dimethoxyaniline → 4-*o*-nitrobenzeneazo-1-amino-7-naphthol is a black dye. E. S.

Chrome Azo Dyes. J. R. Geigy A.-G. *B.P.* 637,934.

Metachrome dyes are made by coupling a diazotised 2-aminophenol-6-sulphonic acid, subst. in the 4-position by an aliphatic or *cyclo*aliphatic radical of 4–8 C, with a 1-carbalkoxyamino-7-naphthol. They give redder greys than those of the similar dyes of *B.P.* 588,771 (cf. J.S.D.C., **63**, 358 (1947)), which contain Cl, instead of the alkyl or *cyclo*alkyl radical, in the 4-position. An example is the monoazo dye 4-*tert.*-amyl-2-aminophenol-6-sulphonic acid → 1-carbomethoxyamino-7-naphthol. E. S.

Substantive Disazo Dyes. K. A. J. Chamberlain, N. H. Haddock, and I.C.I. Ltd. *B.P.* 638,399.

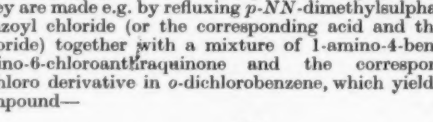
Clarets are produced on cellulosic fibres by applying the disazo compounds 4-aminoazobenzene-4′-sulphonic acid (or the 2′:3-dimethyl homologue) → 2-*m*-amino-*p*-methylbenzoylamino-5-naphthol-7-sulphonic acid, and diazotising and developing on the fibre with *β*-naphthol. The dyes discharge better than the similar compounds described in *B.P.* 586,663 (J.S.D.C., **63**, 277 (1947)) where 2-*m*-amino-*p*-methoxybenzoylamino-5-naphthol-7-sulphonic acid is used as an end component. E. S.

Anthraquinone-nitriles— Dyes for Cellulose Esters and Ethers. G. W. Seymour, C. E. Hieserman, and Celanese Corpn. of America. *U.S.P.* 2,496,414.

Blue dyes for cellulose acetate, fast to gas fumes, are obtained by partly hydrolysing 1-amino-4-substituted-aminoanthraquinones which contain in the 2- and/or 3-positions cyano groups, at 140–150°C., with buffered aqueous solutions of pH 8–9. The reaction, carried out under pressure, consists in replacing the 1-amino by a 1-hydroxy group. Sodium bicarbonate is a suitable buffer salt, and adding diatomaceous silica to the reaction mixture causes the product to form in pellets, easily separated by pouring on to an 80-mesh sieve. R. K. F.

Acylamino – Anthraquinone – Sulphonamides— Vat Dyes. Ciba Ltd. *B.P.* 635,924.

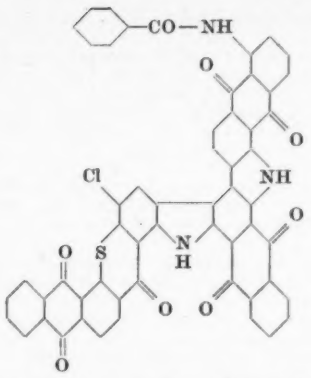
1-Acylamino-4-*p*-sulphamylbenzoylaminoanthraquinones containing halogen in the 6- or 7-position are pink vat dyes. They are made e.g. by refluxing *p*-*NN*-dimethylsulphamylbenzoyl chloride (or the corresponding acid and thionyl chloride) together with a mixture of 1-amino-4-benzoylamino-6-chloroanthraquinone and the corresponding 7-chloro derivative in *o*-dichlorobenzene, which yields the compound—



R. K. F.

Anthraquinone – Thioxanthone – Dicarbazoles — Vat Dyes. F. Max, D. I. Randall, and General Aniline & Film Corpn. *U.S.P.* 2,495,014.

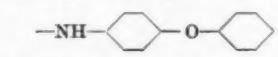
Brown to violet vat dyes are made by condensing a 6′-halogenoanthraquinone-thioxanthone with a 1:5- or 1:4-diaminoanthraquinone and then further condensing the product with a 1-halogenoanthraquinone. The resulting anthrimide is finally cyclised to the dicarbazole. Thus the dye—



is prepared by condensing anthraquinone-2:1(*S*)-1′:2′(*S*)-3′:6′-dichlorothioxanthone with 1:4-diaminoanthraquinone at 205°c. for 4 hr. in presence of sodium carbonate and copper acetate. 1-Chloro-5-benzoylaminoanthraquinone is then added, and the reaction continued for 15 hr. The product is cyclised by heating at 90°c. with aluminium chloride in nitrobenzene. R. K. F.

Anthrapyrimidine Derivatives—Acid Dyes. J. Wardleworth and I.C.I. Ltd. *B.P.* 635,104.

Red acid dyes are obtained by sulphonating in sulphuric acid at 0–25°c. 2-aryl-1′:9′-anthrapyrimidines containing in the 6-position an –NH·R·X·Ar group (R = arylene; X = –O– or a direct link), e.g.—



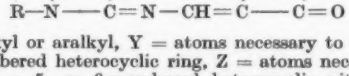
R. K. F.

Benzeneazophthaloylcarbazoles — Acid Dyes. F. Lodge, J. Wardleworth, and I.C.I. Ltd. *B.P.* 635,955.

Brown acid dyes are obtained by sulphonating 9-benzeneazo-1′:2′-phthaloylcarbazoles. Thus 1-benzoylamino-2-methyl-4-*p*-benzeneazoanilinoanthraquinone is cyclised to the carbazole by heating at 160°c. in a mixture of aluminium chloride, sodium chloride, and sodium *m*-nitrobenzenesulphonate. After separating by pouring into iced dil. HCl, filtering, and treating with aqueous sodium dichromate, the product is sulphonated in 20% oleum at 50–55°c. R. K. F.

Aza*mero*cyanine Dyes. T. R. Thompson and General Aniline & Film Corpn. *U.S.P.* 2,496,899.

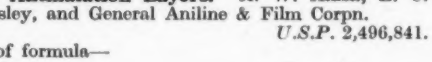
Dyes of formula—



(R = alkyl or aralkyl, Y = atoms necessary to complete a 5-membered heterocyclic ring, Z = atoms necessary to complete a 5- or 6-membered heterocyclic nitrogenous nucleus) are obtained by refluxing, in presence of a basic condensing agent and a tertiary base as catalyst, 1 mol. of a 2-amino heterocyclic nitrogenous quaternary salt with 1 mol. of a 5-membered heterocyclic rhodanine derivative having a reactive acetanilido group linked to a C of a monomethin chain adjacent to a keto group. C. O. C.

Silver Salts of Azanol Dyes for Photographic Filters and Antihalation Layers. A. W. Anish, L. C. Hensley, and General Aniline & Film Corpn. *U.S.P.* 2,496,841.

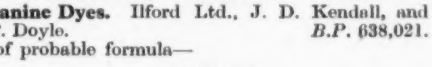
Dyes of formula—



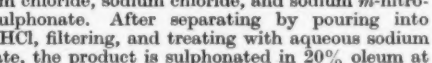
(A = atoms to complete a 5- or 6-membered heterocyclic nucleus; $n = 1$ or 3; N·X·N = radical of a primary diamine of < 15 C) have valuable sensitising properties and also form stable heavy-metal salts. C. O. C.

***mero*Cyanine Dyes.** Ilford Ltd., J. D. Kendall, and F. P. Doyle. *B.P.* 638,021.

Dyes of probable formula—



(R^1 = alkyl, hydroxyalkyl, aralkyl, or hydroxyaralkyl; R^2 = H or a hydrocarbon radical; R^3 = alkyl or aralkyl; D^1 = residue of a 5- or 6-membered heterocyclic nitrogenous ring; D^2 = residue of a heterocyclic ketomethylene ring; $n = 0$ or 1; X = an anion), which are also intermediates of dyes, are obtained by treating a *mero*cyanine dye of formula—



with an acid and a compound of formula $HC(SR^3)_3$ in presence of a carboxylic acid or anhydride as solvent for the reactants. *B.P.* 638,023.

A cyanine dye of formula—

(R^1 and R^2 = same or different alkyl, hydroxyalkyl, aralkyl, or hydroxyaralkyl; D^1 and D^2 = same or different residues of 5- or 6-membered heterocyclic nitrogenous rings; $n = 0$ or 1; $x = 1$ or 2; A = an anion) is treated with an acid HX and a compound $HC(SR^3)_3$ (X = anion, R^3 = alkyl or aralkyl) in presence of a carboxylic acid or anhydride as solvent to yield products of formula—

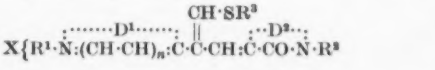
B.P. 638,022.

Cyanine dyes of the second formula in the preceding abstract (in which $n = 0$; $x = 1$; and D^1 and D^2 = same or different residues of a 5-membered heterocyclic nitrogenous ring) are treated with a hydrolytic agent to yield dyes of formula—

B.P. 638,024.

Trinuclear polymethin dyes are obtained by treating products of *B.P.* 638,023 (above) with a heterocyclic nitrogenous compound containing a reactive methylene group. *B.P.* 638,047.

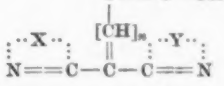
*mero*Cyanine dyes of formula—



(Q = O or S) yield trinuclear polymethin *mero*cyanine dyes when treated with a heterocyclic nitrogen compound containing a reactive methylene group. C. O. C.

Hydroxy Heavy-metal Salts of Trinuclear Iminol Cyanine Dyes. A. W. Anish and General Aniline & Film Corpn. *U.S.P.* 2,496,843.

Dyes of formula—



(M = H or a heavy metal; X and Y = same or different atoms necessary to complete a heterocyclic ring; Z = atoms necessary to complete a 5- or 6-membered heterocyclic nucleus) are useful as photographic sensitisers and as filter and anti-halation dyes. C. O. C.

Cadmium or Cadmium-Selenium Red Pigments. G. C. Marcot and American Cyanamid Co. *U.S.P.* 2,496,587.

A mixture of cadmium sulphide, metallic selenium, and cadmium oxide (or a compound which yields it when calcined), containing no free sulphur and having mol. ratios of selenium : cadmium oxide of 3 : 2 and of cadmium sulphide : selenium of not < 1 : 3, yields on calcination pigments ranging in colour from bright orange to a dark maroon and containing both CdS and CdSe.

U.S.P. 2,496,588.

A method of preparing a composite mixture of controlled flux content which on calcination yields a pigment of optimum quality is described. C. O. C.

Calcium Carbonate Pigment. H. R. Rafton and Raffold Process Corpn. *U.S.P.* 2,498,005.

Dry or damp natural or artificial calcium carbonate is pounded with striking surfaces mounted on a rapidly rotating element. The products disperse readily in liquids without grinding. They also require less adhesive when used in coatings for paper or in water paints and have a lower oil absorption than previously known calcium carbonate pigments. C. O. C.

Lead Silicate. Goodlass Wall & Lead Industries Ltd. and N. J. Read. *B.P.* 637,622.

Hydrated lead silicate, of good stability to light, of fine and uniform particle size, of good staining resistance, and of good storage stability and whiteness when used as a pigment in paints, is obtained by grinding a mixture of lead monoxide or lead hydroxide and silicic acid in water in presence of an acid catalyst. C. O. C.

Red-fluorescing Magnesium Titanate Phosphors. British Thomson-Houston Co. Ltd. *B.P.* 639,086.

A phosphor which emits red fluorescence under ultra-violet radiation is obtained by heating a dry mixture of 2–4 mol. of MgO and 1 mol. of TiO_2 with 10% by weight of AlF_3 and enough of a manganese compound to yield 0·01–0·1% by weight of MnO in air at 1000–1200°C. C. O. C.

Carbon Black. W. B. Wiegand, H. A. Braendle, and Columbian Carbon Co. (I, p. 486.)

Hypochlorite Oxidation of Cellulose in presence of Mixtures of certain Vat Dyes—II. G. M. Nabar and J. A. Rathod. (VI, p. 495.)

V— PAINTS; ENAMELS; INKS

Theory of the Printing of Lithographic Inks. I—Effect of Ink Viscosity and Pigment Flocculation. II—Greasing and Theory. E. Carman. *Amer. Ink Maker*, **28**, (2), 25–27, 55; (3), 36–38, 65 (1950): *Chem. Abs.*, **44**, 5115 (10th June 1950).

Viscosity, pigment flocculation, and greasing, the factors in the functioning of lithographic ink, are discussed in terms of interfacial relations among pigment particles, vehicle, additives, and the lithographic plate. C. O. C.

Use of Amine Additives to prevent Drying Loss on Aging. A. C. Zettlemoyer and D. M. Nace. *Ind. Eng. Chem.*, **42**, 491–495 (March 1950).

Of various nitrogenous compounds tested, including hæmin and *o*-phenanthroline complexes of drier metals, DMP-30 (2:4:6-tri(dimethylaminomethyl)phenol), I, was found to be the most practical and most effective in preventing loss of drying on aging of printing inks pigmented with alumina hydrate lakes. Excess I tends to inhibit drying and accelerate livering, and only 1–2% on the wt. of the pigment should be used. I is almost completely adsorbed by the pigment, but the amount of cobalt absorbed is not reduced by its presence. It is considered that I is effective because it changes the acidic nature of the pigment surface. W. K. R.

PATENTS

Daylight-fluorescent Pigment Compositions. J. L. Switzer and R. C. Switzer. *U.S.P.* 2,498,592.

A daylight-fluorescent composition comprises a daylight-fluorescent dye dissolved in a solid polymerised thermoset resin. The maximum weight of dye varies from 0·025 g. for yellow-greens to 0·015 g. for reds per c.c. of resin. This coloured resin is then dispersed in a transparent resinous vehicle. The resulting composition is applied to the materials to be treated so that the weight of dye per sq. cm. of the treated surface does not exceed 0·0005 g. for each spectral waveband of light projected. C. O. C.

Water-emulsion Paint. L. L. Ryden and Dow Chemical Co. *U.S.P.* 2,498,712.

Water-emulsion paints which yield films which do not readily putrefy and which after drying resist abrasion consist of aqueous dispersions of a copolymer of a mixture of polymerisable unsaturated hydrocarbons and 40–60 mol.% of an aliphatic conjugated diolefin together with a pigment. C. O. C.

Vehicle for Printing Inks. H. A. Seil and H. Cole. *U.S.P.* 2,499,004.

Two parts by weight of incompletely polymerised resin dissolved in 1 part of an aliphatic hydrocarbon solvent non-volatile at room temperature is used. The resin is formed by heating 2·75 mol. phthalic anhydride, 1–1·5 mol. vegetable-oil fatty acid, and a polyhydric alcohol of OH-value equal to 3·5 mol. glycerol, in which the alcoholic OH groups are the sole reactive groups, to 230°C. in 1 hr. and maintaining that temperature for a further 3 hr. 15 min. This gives a heat-setting ink which is stable for long periods and which does not dry or cake on the press. C. O. C.

Compositions containing Cerium Acetate—Spot-proofing Agents for Rayon Hose, Components for Paints, etc. C. E. Griffin. (III, p. 488.)

Stable Aqueous Dispersions of Resins by using Ammonium Alginate. W. C. Mast and U.S. Secretary of Agriculture. (III, p. 489.)

Influence of Differently Coloured Light on Rate of Drying of Linseed Oil. E. Stock. (X, p. 500.)

VI—FIBRES; YARNS; FABRICS

Review of Research and Development in the Field of Textiles during 1949. Textile Research Institute and Textile Foundation. *Text. Research J.*, **20**, 317–360 (May 1950).

This paper is a non-critical review of the literature published in 1949 relating to textile science and technology, both in U.S.A. and abroad. The structure and physical and chemical properties of natural, regenerated, and synthetic fibres are reviewed, and some papers on dyeing and the properties of dyes are mentioned. In development fields, scouring, bleaching, dyeing, printing, and finishing progress is reviewed. There are 826 references to the literature. P. C.

Crystallinity of Cellulose and its Significance for the Fibre Properties. K. Ward, Jr. *Text. Research J.*, **20**, 363–372 (June 1950).

The nature and degree of crystallinity of cellulose are discussed with particular reference to cotton cellulose and to the interrelation between crystallinity and fibre properties. Four main aspects of crystallinity are considered, viz. the nature of the crystal lattice, the percentage of crystalline material, the size of the crystallites, and the orientation of the crystallites. It is considered that a planned analysis of covariance between these factors and the important physical properties of cotton would be desirable, but in the absence of this analysis it is still possible to show correlations between these parameters and the main fibre properties. Such correlations are considered in detail, using the available published literature. P. C.

Hydrolysis and Crystallisation of Cellulose. O. A. Battista. *Ind. Eng. Chem.*, **42**, 502–507 (March 1950).

The effect of time on the weight loss and degree of polymerisation (D.P.) of native and regenerated celluloses has been studied under mild (5 N-HCl at 5°, 18°, and 40°C.) and drastic (2·5 and 5 N-HCl at the boil) hydrolysing conditions. The weight loss is shown to depend on (1) the rate of hydrolysis and (2) crystallisation and crystal growth, which appear to occur simultaneously with the hydrolysis. Smaller weight loss occurs under mild hydrolysis for a long period than under a short drastic hydrolysis, although the D.P. approaches the same limiting value in each case. A mild hydrolysis pretreatment, which favours the crystallisation of disorganised chains, reduces appreciably the weight lost on subsequent drastic hydrolysis. Reaction mechanisms are proposed to explain these results. Crystallisation on hydrolysis is more pronounced with regenerated than with native celluloses. Hydrolysis with boiling 2·5 N-HCl for 15 min. is recommended as the optimum condition for measuring weight loss and limiting D.P. W. K. R.

Fine Structure of Cellulose. B. G. Rånby and E. Ribi. *Experientia*, **6**, 12–14 (1950): *Chem. Abs.*, **44**, 4677 (25th May 1950).

The frequency curves of many cellulose samples contain mean degree of polymerisation (D.P.) maxima of 70–100 and 200, in addition to those of 1000–2000, glucose units. After profound degradation, most of the cellulose has a D.P. of

about 100 (molecular length 500 A.). This tendency is thought to be caused by the crystalline nature of cellulose walls. The crystalline areas, the micelles, have been isolated as an aqueous colloidal solution, and electron-microscopic examination showed their size to be 500–600 × 50–100 A. Examination of cellulose fibre after ultrasonic treatment shows it to be composed of elementary fibrils (micellar strings) of the same thickness as micelles. C. O. C.

Hypochlorite Oxidation of Cellulose in presence of Mixtures of certain Vat Dyes—II. G. M. Nabar and J. A. Rathod. *J. Sci. Ind. Research* (India), **8 B**, (9), 154–156 (1949): *Chem. Abs.*, **44**, 4673 (25th May 1950).

Reduced Ciba Blue 2B (I) and the reduced mixed dyeings show maximum oxygen consumption and maximum cuprammonium fluidity of the treated dyeings at pH approx. 6·3. Reduced Cibanone Orange R (II) dyeings show the maximum at approx. pH 7·3. In presence of reduced I, reduced II loses its identity, as shown by the shift in the pH for maximum oxygen consumption by the mixed dyeings. The influence of I on the accelerating action of II on the oxidation of cellulose decreases with decreasing pH of the NaOCl solution. I exerts some influence on the reduction potentials of II. C. O. C.

Sub-Cuticle Membrane—A Recently Discovered Morphological Component of the Wool Fibre. P. Alexander and C. Earland. *Text. Research J.*, **20**, 298–300 (May 1950).

When wool is treated with a cold aqueous solution of peracetic acid for 25 hr., more than 90% of the cystine present is oxidised and the wool becomes freely soluble in dilute ammonia except for a resistant fraction comprising 7–10% of the whole. This fraction is membrane-like in form and is believed to represent the "sub-cutis", a sheath-like layer between the scales and the cortical cells in the fibre. The membrane is continuous, is resistant to chlorine solutions of any pH, and is a protein. It contains no cystine, but some cysteic acid has been found. All the amino acids present in normal wool have been detected. Its resistance to alkali is similar to that of untreated wool. Its increased resistance to chemicals points to the existence of a covalent linkage, e.g. an ether linkage, not present in the rest of the wool. It may act as a selective membrane which in alkaline solution will have a negative charge and retard the diffusion of anions into the fibre. P. C.

Rate of Acid Sorption by Wool Fibres. J. Lindberg. *Text. Research J.*, **20**, 381–384 (June 1950).

The rate of diffusion of mineral acids into wool fibres has been measured by dispersing short fibres (1–3 mm. long) in acid solutions and determining the decrease in concentration by means of a conductivity cell. Using the treatment developed by Crank (*Phil. Mag.*, **38**, 794 (1947); **39**, 140, 362 (1948)) for the sorption of a solute from a solution by a sorbing medium in plane sheet or cylinder form, the diffusion constant was calculated. The experimental curves of diffusion against time showed good agreement with the theoretical curves. It is shown that when wool is treated with substances known to impair the epicuticle of the fibre, e.g. alcoholic caustic potash, the rate of diffusion of acids into the fibre is increased. P. C.

Frictional Properties of Wool and Nylon Fibres. G. King. *J. Textile Inst.*, **41**, T 135–T 144 (April 1950).

The frictional coefficients for wool and nylon fibres rubbing on glass, casein, ebonite, sheep's horn, and cow's horn surfaces have been measured using a slip stick technique. The effect of surface roughness on the directional frictional effect has also been examined, and the relation between frictional coefficient and normal pressure is discussed. The action of swelling agents on the frictional coefficients of wool and nylon suggests that the elasticity of the rubbing materials and their coefficients of friction are closely related. A. S. F.

Structure of Alginate Fibres. E. E. Tallis. *J. Textile Inst.*, **41**, T 151–T 157 (April 1950).

The chemical and X-ray evidence used in determining the structure of alginic acid and its derivatives is reviewed chronologically. Alginic acid fibres are highly crystalline and well oriented, whereas calcium alginate fibres are less crystalline and only moderately oriented. Beryllium and chromium alginates are of interest owing to their resistance to soap solutions. Metallic alginate fibres are flame-resistant because of their high metal content, but the metal ions bring about cross-linkages between alginic acid chains, with the result that extensibility is limited. A. S. F.

Stabilisation of Zein Filaments — Curing with Formaldehyde in Acidic Non-aqueous Media. C. B. Croston. *Ind. Eng. Chem.*, **42**, 482–484 (March 1950).

Zein fibres may be stabilised by curing under essentially anhydrous conditions by treatment with a mixture of formaldehyde or paraformaldehyde, a strong acid catalyst, and an inert solvent (e.g. dioxan, toluene, white spirit) at approx. 100°C. The reaction is rapid and produces irreversible cross-bonds. The treatment is much more effective than the normal aqueous formaldehyde cure, and the efficient stabilisation is evident in the reduction of shrinkage and retention of strength after dyeing at the boil in an acid bath. W. K. R.

Amilan Fibres. K. Hoshino and S. Funami. *J. Soc. Org. Synthetic Chem.* (Japan), **7**, 2–3 (1949): *Chem. Abs.*, **44**, 3895 (10th May 1950).

Phenol was hydrogenated in presence of nickel to *cyclo*hexanol, then dehydrogenated to *cyclo*hexanone in presence of copper, converted to the oxime with hydroxylamine, then by Beckmann rearrangement to ε-caprolactam, which was hydrolysed to $NH_2{\cdot}[CH_2]_5{\cdot}COOH$ and then dehydrated and polymerised to $[NH{\cdot}[CH_2]_5{\cdot}CO]_m$ (Amilan, m = 100–150). This was spun, drawn, and baked into fibres and filaments useful as bristles and for making shoe laces, etc. C. O. C.

PATENTS

Cyanoethyl Derivatives of Cellulose. J. P. Hollihan, Jr., S. A. Moss, Jr., and American Viscose Corpn. *U.S.P.* 2,499,501.

Acrylonitrile and viscose are mixed at 40°C. to yield a cyanoethyl cellulose xanthate in which the cyanoethyl groups are distributed uniformly along each of the molecular chains at all portions of the cellulose xanthate. The product is extruded, before hydrolysis of the cyano-ethyl groups occurs, into an acid coagulant. C. O. C.

Strengthening Artificial Protein Filaments. D. Traill and I.C.I. Ltd. *B.P.* 639,342.

Artificial insolubilised protein filaments are strengthened by treatment under tension with an aq. soln. of an ionisable mercuric salt. In one example filamentary tow from groundnut protein, spun and hardened in the usual way with acid saline formalin, is stretched to the maximum in 3% aq. mercuric acetate and 0·1 N. acetic acid for 30 min. at 70°C., dried at 110°C., washed, and redried at 110°C. J. W. B.

Strengthening Artificial Protein Filaments. G. K. Simpson, J. Brooks, and I.C.I. Ltd. *B.P.* 639,363.

Insolubilised fibre is strengthened by aftertreatment in an aq. soln. of at least one uranyl salt, e.g. by stretching in a soln. of 3% uranyl acetate and 0·1 N. acetic acid for 30 min. at 70°C. The tensile strength is increased by 80%. J. W. B.

Polyamides. Wingfoot Corpn. *B.P.* 637,926.

Addition to *B.P.* 634,172 (J.S.D.C., **66**, 390 (July 1950)). Fibre-forming polyamide condensation polymers can also be prepared by heating the amino acids already specified with polymeric carboxylic acids or their derivatives, e.g. polyacrylic acid. W. G. C.

Insolubilising Linear Hydroxylated Polymers by Titanation. Du Pont. *B.P.* 637,867.

Synthetic linear hydroxylated polymers, e.g. a hydrolysed vinyl ester–ethylene interpolymer, are made resistant to hot water by orienting a filament by drawing at 200–250°C., heating while relaxed below 225°C. till the fibre shrinks 8–40%, swelling in a liquid, and then treating with an insolubilising agent which can react with the hydroxyl groups of the polymer. In addition to formaldehyde, amide–formaldehyde compounds, and the known cross-linking agents, the water-insolubilising agent may be an aqueous solution of an acidic quadrivalent titanium salt; e.g. the relaxed and swollen hydroxylated polymer is treated with 32% titanium sulphate solution at 67°C. for 1 hr., rinsed in 95% alcohol for 10 sec., and neutralised with ammonia. The treated yarn shrank only 9% in boiling water, and could be ironed at higher temp. than the untreated fibre. W. G. C.

Plasticisers for Polyamides. G. R. Sido and Monsanto Chemical Co. *U.S.P.* 2,499,932.

The reaction products of alcohols with *N*-hydroxyalkylarylsulphonamides are compatible plasticisers for nylon. C. O. C.

Solvents for Polyacrylonitrile. R. Hill, R. G. A. New, S. M. Todd, and I.C.I. Ltd. *B.P.* 638,331.

Organic compounds having 4 or 5 atoms linked together to form a single ring, the components of the ring including at least one O and at least one CO, the other components being chosen from CH_2 and CH:CH, e.g. ethylene carbonate or succinic or maleic anhydride, are excellent solvents for polyacrylonitrile. The solutions are suitable for the production of filaments. C. O. C.

Polyacrylonitrile Fibres and Solvents for them. G. E. Ham and Monsanto Chemical Co. *U.S.P.* 2,498,605.

Acid anhydrides having unsubstituted 5-membered rings, e.g. maleic or succinic anhydride, are excellent solvents for polymers and copolymers of acrylonitrile. Such solutions may be used for preparing high-tenacity fibres by extrusion methods. C. O. C.

Acetonitrile as Solvent for Acrylonitrile Polymers. D. W. Chaney and American Viscose Corpn. *U.S.P.* 2,496,267.

Copolymers of 65–80 mol. % of acrylonitrile and 35–20 mol. % of vinyl acetate are soluble in acetonitrile at room temperature to give solutions from which tough, flexible, colourless filaments can be spun. C. O. C.

Increasing the Dye Receptivity of Polymeric Nitriles. H. W. Arnold and Du Pont. *U.S.P.* 2,497,526.

Polymers of unsat. nitriles of formula H_2C:CR·CN (R = H or Alk), e.g. polyacrylonitrile, are treated either alone or in solution at 20–180°C. with 1–60% by weight of a hydrazine until the dye receptivity of the polymers has been substantially increased. Polyacrylonitrile fibres treated in this manner show marked increase in affinity for acid dyes. C. O. C.

Heat Treatment of Vinyl Halide–Acrylonitrile Polymer Fibres. T. A. Feild, Jr., and Union Carbide & Carbon Corpn. *U.S.P.* 2,499,477.

Stretching fibres of vinyl halide–acrylonitrile polymers at least 200% while at 100–250°C. imparts increased tensile strength and true elasticity. C. O. C.

Fibrous Sheets and Webs. Courtaulds Ltd., F. Happey, and J. H. Grimes. *B.P.* 638,591.

Cellulose fibres are incompletely esterified with an organic acid or anhydride, and carded into a web which either singly or in layers is treated with a solvent, e.g. methylene chloride, to plasticise the surface-esterified fibres. Light pressing followed by solvent evaporation causes adhesion into a soft compact web, suitable for cleansing purposes, which is not spoiled by prolonged immersion in water. J. W. B.

Reddening of Sulphite Pulp. II— Chemical Nature of the Reddening Component. E. Adler and S. Häggroth. (XI, p. 501.)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Behaviour of Dyed Materials on Washing. H. Holderegger. *Textil-Rund.*, **5**, 191–197 (May), 232–237 (June), and 269–277 (July 1950).

A detailed study of the behaviour of dyed cotton and wool on washing. The influence of soap concn., liquor ratio, temp., and time on staining of white material and on loss in depth are assessed by means of the Pulfrich photometer and expressed graphically. The fastness to washing of dyeings on damaged and undamaged wool is compared. The effect of wetting-out agents, soda, and other electrolytes on the washing liquor is examined. The improvement in washing fastness by aftertreatment with synthetic resins of the melamine–formaldehyde or melamine–urea type is found to be caused by reduced swelling of the fibres during the washing process. B. K.

Alkarylsulphonate – Builder Mixtures — Detergent Properties. R. C. Merrill and R. Getty. *Ind. Eng. Chem.*, **42**, 856–861 (May 1950).

The soil-suspending power of various alkaline builders was assessed by measuring their ability to prevent the deposition of iron oxide, ilmenite, and raw umber on to cotton cloth. Sodium silicates and sodium phosphates were more effective than sodium carbonate and sodium hydroxide. Sodium dodecylbenzenesulphonate suspended more iron oxide and less raw umber than the builders, less ilmenite than the phosphates or silicates, but more than sodium carbonate and hydroxide. Certain silicate–phosphate mixtures appeared to show synergism in preventing soil deposition. Soil removal properties were assessed by measuring the cleaning of cotton cloth soiled with three artificial mixtures. The amount of soil removed and the relative efficiency of detergent–builder mixtures varied considerably according to the type of soil present. Generally, detergent–builder mixtures gave equal or better cleaning than the detergent alone, at lower cost. With one type of soil, alkarylsulphonate–tetrasodium pyrophosphate, or sodium meta- or sesqui-silicate, showed large synergistic effects. W. K. R.

Occurrence of Soluble Wool-substance as a result of the Sulphuric Acid Carbonising Process. J. Bauer. *Amer. Dyestuff Rep.*, **39**, P122–P128 (20th Feb. 1950).

In carbonising, loss of wool substance occurs owing to the removal of degradation products during rinsing and neutralising. In commercial practice this loss is of the order of 1–4%, fine wools suffering a greater loss than coarse wools. It is shown that the extent of the loss is influenced by the strength of the sulphuric acid used and by the time and temp. of drying. Carbonised wool has a lower nitrogen content than the original, and the substance removed consists of low-mol.wt. proteins, the nitrogen of which is mostly in amino form, produced by acid hydrolysis of the wool protein. Repeated carbonising results in progressive loss in weight. W. K. R.

Loss of Weight in Kier-boiling, Width Contraction in Bleaching, and Length Increase in Finishing–Calendering Processes. N. H. Shah. *Indian Textile J.*, **60**, 492–495 (March 1950).

Works-scale experiments are carried out in the finishing of cotton goods. Variations in width, length and weight of piece, and in tensile strength, count and twist of component yarns are discussed, together with reasons for these variations and possible methods of process control. J. W. B.

PATENTS

Controlling Felting of Wool Goods during Washing or other Wet Processing. J. M. Preston. *B.P.* 639,576.

Increasing the viscosity of the scouring or other liquor leads to diminution of felting; it is noticeable at 15 centipoises, and at 300 centipoises felting is practically eliminated. Any suitable substance, e.g. starch, sodium alginate, tragacanth, methyl cellulose, or polyvinyl alcohol may be used to cause the increase in viscosity. C. O. C.

Activating the Oxidising Power of Chlorite Solutions. Solvay & Cie. *B.P.* 639,235.

The oxidising power of chlorite solutions is activated by adding enough of a finely divided Group V or VI metalloid or of carbon to acidify the solution by forming, at the expense of a small quantity of chlorite, the acid corresponding to the metalloid used, this acid then decomposing the chlorite to liberate ClO_2. The metalloid may be added either in the free state or as a compound, e.g. thiocyanate, which simultaneously liberates the free metalloid and lowers the pH of the chlorite solution. C. O. C.

Peroxide Bleaching. "Solo" Závody na Zápalky N.P. *B.P.* 637,928.

The materials are impregnated with an aqueous solution of hydrogen peroxide, e.g. with a 4–8% solution at not > 50°C., and are then steamed so as to bring their temperature to 90–95°C. in 1 min., after which gaseous ammonia is admitted to the steaming chamber. The ammonia acts as a catalyst and brings about complete bleaching in 30 sec. Admission of steam to the chamber is continued during this 30 sec. and for 1 min. afterwards. C. O. C.

VIII— DYEING

Hydron Blue Dyeing. K. A. Rinneberg. *Textil-Praxis*, **5**, 247–251 (April), 309–313 (May 1950).

Practical recommendations and recipes are given for applying Hydron Blue type dyes to loose cotton, sliver,

yarn, and piece. Continuous dyeing of pieces by the direct, pigment-pad, and vat-acid processes is described. F. A.

Method of Evaluating Protective Colloids for Vat Dyeing. P. Wengraf. *Amer. Dyestuff Rep.*, **39**, 449–451 (10th July 1950).

Translation from *Textil-Rund.*, **4**, 328–332 (Sept. 1949): cf. J.S.D.C., **66**, 83 (Jan. 1950).

The Vat Acid Process. J. A. Heyder and G. N. Sandor. *Textil-Rund.*, **5**, 179–186 (May 1950).

The application of the vat acid process to piece goods, cheeses, warps, and hank yarns is described together with bulk recipes. The addition of a dispersing agent is recommended to prevent precipitation, and this should be stable over the pH range 4–11. The following products have proved satisfactory — formaldehyde–naphthalenesulphonic acid condensates (Setamol WS, Belloid TD), purified ligninsulphonic acids (Cellex, Dekol, etc.), and sulphonated aliphatic alcohols. The vat acid soln. reacts weakly acid, exhibits a fine colloidal dispersion of particle size usually $< 0{\cdot}01\mu$., is immediately converted into the sodium leuco compound with NaOH and hydrosulphite, and lacks substantivity. Comparison with the pigment padding process shows the following advantages of the vat acid technique— independence of dye particle size, improved levelling and penetration especially with certain types of piece goods, easier application to cheeses and beams, and quicker vatting. The pigment padding process, on the other hand, has the advantage of ease of handling of the vat pigment, and also there is no limitation with respect to depth of shade which can be obtained. B. K.

Sorption of Acid Dyes on Nylon. F. C. McGrew and A. K. Schneider. *J. Amer. Chem. Soc.*, **72**, 2547–2553 (June 1950).

When nylon is dyed with acid dyes at pH 3–4 a salt-type linkage is formed between the basic amine ends of the polymer chain and the sulpho groups of the dye. The sequence of acid dyes in which each dye will replace on nylon from mixed solution any dye of lower order, but cannot be readily replaced in turn by any such dye of lower order, coincides exactly with the arrangement of the dyes in order of diminishing affinity for nylon. This explains why adsorption of acid dyes on nylon from mixtures is accompanied by more irregularities than in the case of wool, for the smaller number of available basic sites in nylon leads to competition between the dyes. C. O. C.

Equilibria of the Dyeing of Nylon with Acid Dyes. W. R. Remington and E. K. Gladding. *J. Amer. Chem. Soc.*, **72**, 2553–2559 (June 1950).

Gilbert and Rideal's explanation of the mechanism of absorption of acids by fibrous proteins (*Proc. Roy. Soc.*, **A 182**, 335 (1944)) accounts for the absorption of monobasic acid dyes by nylon. The acid-titration equation for nylon derived on the basis of this mechanism differs from the corresponding equation for wool developed by Gilbert and Rideal, by the inclusion of a term taking account of the excess of carboxyl over amino end-groups. Application of an appropriately rearranged form of the acid-titration equation permits graphical analysis of the equilibrium absorption data. The experimental data for single dyes and mixtures fit the equation satisfactorily. This analysis yields a precise value for the amine end content of nylon which is the practical upper limit for dyeing with acid dyes. Absorption of dye from solutions of low pH is accompanied by hydrolytic rupture of principally non-terminal amide groups, with consequent production of additional dyeing sites. This occurs at pH within the range of normal dyeing practice, and accounts for the degradation of nylon when excessive amounts of acid dyes are applied from strongly acid solutions. C. O. C.

Dyeing of Piece Goods made from Reclaimed Fibres. E. Smith. *J. Textile Inst.*, **41**, P 208–P 218 (May 1950).

Methods of identification and separation of fibre mixtures are briefly discussed. Stress is laid on the difficulties of dyeing wool containing small amounts of acetate rayon, owing to the affinity of wool for dispersed dyes. Wool containing nylon is considered in detail, and lists are provided of dyes having low and high affinities for nylon. The approx. percentage of each fibre should be known, and stripping, if necessary, is carried out by the formaldehyde-sulphoxylate–acetic acid process. Level dyeing is obtained by selecting mixtures of two dyes or two groups of dyes; while for application of chrome dyes the afterchrome process is recommended, modified by adding 3–4% of sodium thiosulphate after the chroming boil, and boiling a further 20 min. By varying the amount of Calsolene Oil HS added from 0·5 to 8%, when using $< 1\%$ of dye, it is possible to decrease the amount of dye going on to the nylon. J. W. B.

Solubilisation of Protein–Dye Precipitates. J. C. Perrone. *Rev. brasil. Biol.*, **9**, 425, 426 (1949): *Chem. Abs.*, **44**, 4525 (1950).

The precipitates formed by adding various cationic dyes to a slightly alkaline solution of egg albumin redissolve when a soap or an anionic alkyl sulphate detergent is added. Cationic and non-ionic detergents have no such action. The soaps and anionic detergents form soluble non-dialysable complexes with the dyes. C. O. C.

Aftertreatment of Substantive Dyeings with Cation-active Compounds. M. Bräuer. *Textil-Praxis*, **5**, 242–244 (April), 305–308 (May 1950).

The properties and uses of cation-active compounds and details for efficient aftertreatment of substantive dyeings are outlined. A method for estimating *Fixiermittel A* and absorption curves for this agent on different fibres are given. Premordanting with cation-active agents is described, with special reference to the coloration of acetate rayon with direct and acid dyes. The discussion extends to a consideration of the limitations of the cation-active dye Alcian Blue. F. A.

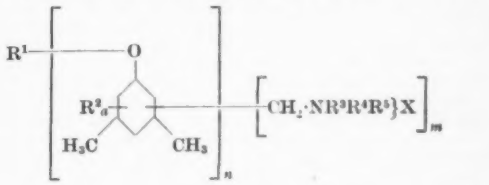
Electrocolouring of Stainless Steel in Aqueous Solutions. C. F. Naylor. *Plating*, **37**, 153–160 (1950): *Chem. Abs.*, **44**, 4350 (25th May 1950).

Steels containing not $< 7\%$ Cr can be coloured brown, blue, bronze, reddish brown, purple, or green by anodic treatment in 25% by vol. H SO_4 containing 60 g. $Na_2Cr_2O_7$ per litre at 70–95°c. and using 0·06 amp./sq. dm. Anodic etching at 8 amp./sq. dm. gives a good surface for uniform colouring. C. O. C.

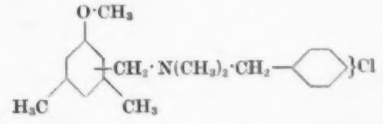
PATENTS

Coupling 3:5-Dimethylphenyl Ethers of Cellulose with Diazonium Salts. L. H. Bock, P. L. de Benneville, and Röhm & Haas Co. *U.S.P.* 2,498,874.

Cellulosic material containing free alcoholic hydroxyl groups is treated with a compound of formula—



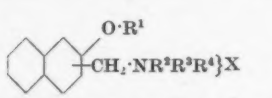
($n = 1$ or 2; $m = 1$ or 2; $a = 0$ or 1; R^1 (when $n = 1$) = a univalent aliphatic hydrocarbon group of 1–18 C; R^1 (when $n = 2$) = a bivalent saturated aliphatic group containing chains of 2–3 C and containing < 7 C; R^2 = alkyl or aliphatic acyl of 1–18 C; R^3 = methyl, ethyl, allyl, methallyl, or benzyl; R^4 and R^5 = methyl or ethyl, or together = a bivalent sat. hydrocarbon chain of 4–5 C or an ether chain which with the N atom forms a heterocyclic ring; or R^3, R^4, and R^5 together = a tervalent unsat. hydrocarbon group which with the N atom forms a heterocyclic ring; X = an anion), e.g.—



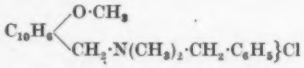
and then with a solution of a diazonium salt, and finally dried and heated to 120–170°c. The resulting coloration is fast to washing and dry cleaning. C. O. C.

Colouring Cellulosic Materials with Diazonium Salts and Naphthyl Ethers. L. H. Bock, P. L. de Benneville, and Röhm & Haas Co. *U.S.P.* 2,498,875.

Cellulosic material containing free alcoholic hydroxyl groups is treated with a solution of a naphthyl ether of formula—



(R^1 = alkyl of 1–18 C; R^2 = methyl, ethyl, allyl, methallyl, or benzyl; R^3 and R^4 = methyl or ethyl, or together = a bivalent sat. hydrocarbon chain of 4–5 C or an ether chain which with the N atom forms a heterocycle; or R^2, R^3, and R^4 together = a tervalent unsat. hydrocarbon group which with the N atom forms a heterocycle; X = an anion), e.g.—



and then with a solution of a diazonium salt, and finally dried and heated at 120–170°c. The resulting colours are fast to washing. C. O. C.

Application of Mixtures of Vat and Onium Dyes. R. Thornton and I.C.I. Ltd. *B.P.* 638,124.

When onium dyes are fixed on textiles they are no longer susceptible to alkaline reducing agents. Thus textiles can be coloured by a mixture of onium and vat dyes by first fixing the onium dye and then reducing and re-oxidising the vat dye. C. O. C.

Use of Boric Acid with Neutral-dyeing Wool Dyes. C. F. Ward, C. S. Groves, and W. E. Saxby (Nottingham) Ltd. *B.P.* 638,176.

Damage to the fibre is avoided when using neutral-dyeing dyes by setting the dyebath with not $< 4\%$ on the weight of the goods of boric acid, this being preferably added to the dyebath and circulated through the goods before the dye is added. This not only protects against damage from alkali present in the goods and/or water, but enables level dyeings to be obtained with dyes hitherto regarded as unlevel-dyeing, and also renders the wool suitable for further treatment, e.g. chlorination. C. O. C.

Dyeing Wool. Ciba Ltd. *B.P.* 637,665.

The material is impregnated with the dye liquor (but not so as to fix the dye in it), and is then brought into sudden contact under atmospheric pressure with a heated acidic solution. The process is applicable to all dyes which have affinity for wool, e.g. acid, direct, and chrome dyes or ester salts of leuco vat dyes. Where dyes require an aftertreatment, it may be carried out immediately after dyeing by this method, or it may be carried out in a correspondingly shortened manner; e.g. chrome dyes and ester salts of leuco vat dyes may be developed by passing them straight from the acidic bath into a strongly heated chrome liquor. C. O. C.

Colouring Cellulose Acetate. T. E. Marchington & Co. Ltd., D. Sutton, and O. Boothby. *B.P.* 639,161.

Cellulose acetate may be dyed or printed with vat dyes in presence of metallic sulphoxylates of aldehydes and ketones with or without addition of a buffer and without the need for swelling agents. Use of a buffer gives increased colour yield with some vat dyes in dyeing and with very many vat dyes in printing. C. O. C.

Dyeing Nylon with Acid Dyes. W. H. Sharkey and Du Pont. *U.S.P.* 2,499,787.

Nylon is dyed in aqueous dyebaths in which the concentration of acid dye is maintained at 0·1–5·0 p.p.m. liquor throughout the dyeing process. Level dyeings are obtained even on nylon, which shows variation in affinity for acid dyes when dyed in the normal manner. C. O. C.

Dyeing Vinyl Halide–Acrylonitrile Copolymers. Carbide & Carbon Chemicals Corpn., T. A. Feild, Jr., and A. G. Schoonover. *B.P.* 639,160.

The materials are dyed above 100°c. with acid, basic, direct, or phthalic anhydride-type dyes, which are then fixed by heating in presence of water or steam at 105–150°c. under 15–20 lb./sq. in., the time of heating, 30 min.–2 hr., varying inversely with the temperature. Level dyeings of excellent colour value and wash fastness are obtained. C. O. C.

Colouring Textiles with Aqueous Pigment Pastes. G. T. Douglas, A. Lowe, S. Robinson, and I.C.I. Ltd. *B.P.* 639,207.

An aqueous paste containing a pigment, a synthetic resin or its components or natural or synthetic rubber, and a compound of formula $R(O{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}A\{X)_n$ (R = an organic residue, A = an aliphatic or heterocyclic tertiary amine group, X = an anion, $n > 1$), e.g. tristearin-tris-(carbamatomethylpyridinium) trichloride, is applied to the textile, which is then steamed or baked at 100–150°c. The coloration obtained is of excellent fastness to rubbing and washing, and the textile has an exceptionally soft handle. *B.P.* 639,294.

Compounds of formula—

$(X\{A{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}O)_mR(O{\cdot}CO{\cdot}NH{\cdot}CH_2OH)_p$

may wholly or partly replace those of the above formula when p and m are integers and only partly when $p > 1$ and $m = 0$. C. O. C.

Rendering Oxide Coatings on Aluminium more adsorptive for Dyes. Aluminum Co. of America. *B.P.* 638,374.

The oxide-coated material is treated with an aqueous solution of an ammonium, aluminium, or magnesium salt of a monobasic acid. C. O. C.

Rendering Oxide Coatings on Aluminium more receptive of Dyes. W. G. Zelley and Aluminum Co. of America. *U.S.P.* 2,496,649.

Oxide coatings produced chemically on aluminium by alkaline treatment are rendered more receptive of dyes by treatment for 5–10 min. in an aqueous solution of 0·5–10% or more of an ammonium salt of a monobasic inorganic or organic acid at $> 170°F$. An exception is NH_4F, which dissolves the coating. C. O. C.

Review of Research and Development in the Field of Textiles during 1949. Textile Research Institute and Textile Foundation. (VI, p. 494.)

IX—PRINTING

Colour Correction with Coloured Couplers. W. T. Hanson. *J. Optical Soc. Amer.*, **40**, 166–171 (1950).

PATENTS

Screen Printing. K. T. Lindahl, C. A. Heintges, J. P. W. Jacobs, and Heintges, Jacobs & Co. *B.P.* 637,812.

The fabric is fed longitudinally in a stepwise manner over the printing table. At the side of the fabric there is a magazine for the screens, from which the screens may be moved across the direction of travel of the fabric to reach the printing position. There is a device to deflect the fabric adjacent to one of the edges of the movement of the screen or ends of the printing table to enable the operator to work from a position close to the edge, so that the squeegee may be moved longitudinally along the fabric. By this means any irregularities are formed as warpwise stripes and so are not as apparent as they would be in the case of irregularities in fabric printed by the squeegee moving across the fabric. C. O. C.

Photographic Colour Prints. Kodak Ltd., F. C. Williams, and F. M. Brown. *B.P.* 639,142.

Multicoloured Subtractive Positive Prints. L. S. Trimble. *B.P.* 639,182.

Colouring Cellulose Acetate. T. E. Marchington & Co. Ltd., D. Sutton, and O. Boothby. (VIII, above.)

Colouring Textiles with Aqueous Pigment Pastes. G. T. Douglas, A. Lowe, S. Robinson, and I.C.I. Ltd. (VIII, above.)

X—SIZING AND FINISHING

Finishing of Fabrics containing Wool and other Fibres. C. S. Whewell. *J. Textile Inst.*, **41**, P 219–P 230 (May 1950).

Neutral scouring of fabrics is necessary if fibres degraded by alkali, e.g. regenerated protein fibres, are present, and oiling with modified mineral oil is useful for alkali-sensitive blends. The greater the amount of wool in wool–Fibro or

wool–Rayolanda blends, the greater is the shrinkage during scouring and milling, though the effect of Rayolanda in reducing shrinkage is smaller than that of Fibro. Variation of staple length of the Fibro or Rayolanda has little effect on the milling shrinkage. Wool–acetate rayon blends shrink much less readily than all-wool materials, and if this is undesirable it may be partly overcome by addition of reagents capable of plasticising the acetate rayon, or by adding softeners. Blending of regenerated protein fibres leads to similar or better milling properties, while incorporation of nylon in fabrics generally reduces their shrinking power. The raising properties of union fabrics are discussed with regard to both the type of fabric mixture and the nature of the raising medium. Some union fabrics, e.g. wool–Rayolanda, may require shrinkproofing, which may be effected without damage by a moderate and well controlled chlorination. Crease-resistance becomes important when more than 50% of Fibro or Rayolanda is present, and may be improved by the standard urea–formaldehyde process. Surface balling-up during use and its enhanced effect in union fabrics are discussed, and methods suggested for its prevention.
J. W. B.

Watering and Embossing— Common Faults [occurring in the Processing of Fabrics] and Practical Remedies. Anon. *Wool Record*, **77**, 1670, 1673, 1674 (1st June 1950).

An account of the various ways in which the faults known as watering, embossing, and imprinting may be caused during the processing of such fabrics as piece-dyed poplins, repps, charmelaines, some serges and gaberdines, and yarn-dyed fabrics of the hopsack, pinhead, and plain weave types, and cloths containing very hard-twisted yarns such as tropicals and frescoes. The removal of these faults from goods in which they occur is discussed and particularly the use of the stocks. C. O. C.

Patent and Literature Survey on Shrinkage and Shrinkage Control of Textile Fabrics. F. D. Horigan and C. R. Sage. ORR 240/50* (PB 98,017).

Microfilm of a survey of the literature published in 1937–47. The items are arranged in chronological order, but there are an author index and a numerical index of patents. C. O. C.

* Photocopies available from T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C.—see J.S.D.C., **66**, 53 (Jan. 1950).

Chemical Reactivity of Wool in relation to Anti-shrink Processes. P. Alexander. *Amer. Dyestuff Rep.*, **39**, P 420–P 430 (26th June 1950).

The structure of wool and the theory of felting are considered briefly. It is shown that oxidation of the disulphide bond alone is insufficient to cause unshrinkability unless treatment is excessive, some other link breakage being necessary. It is suggested that the peptide chain must be broken adjacent to the tyrosine residue. Investigation of the reaction between oxidising agents and the disulphide bond shows that the latter may be divided into two classes of widely different properties, though this division bears no relation to that suggested earlier by Phillips. Differences in environment may cause the variation. The reaction between wool and chlorinating liquors is discussed, the rate-determining step being either diffusion through a film of liquid on the fibre surface or through the fibre itself, and treatment is most even where the latter condition predominates. This is brought about by treatment at pH $> 7{\cdot}5$, where the fibre is negatively charged and hinders the diffusion of OCl^- ions. Efficiency of the permanganate–hypochlorite process is ascribed to the joint effect of two differently acting oxidising agents. J. W. B.

Application of *N*-Carboxy Anhydrides of Amino Acids to Wool. P. Alexander, J. L. Bailey, and D. Carter. *Text. Research J.*, **20**, 385–399 (June 1950).

Various *N*-carboxy anhydrides of amino acids have been prepared and applied to knitted wool fabric to determine their efficiency in reducing felting and milling shrinkage. The conditions of application of *N*-carboxyglycine anhydride in particular were studied in detail, and optimum conditions established. *N*-Carboxy-DL-alanine anhydride was the only other compound that showed any tendency to reduce felting shrinkage. The polymers from the higher amino acids showed no substantivity and had no technical merit. The mechanism of the reaction between *N*-carboxyglycine anhydride and wool has been studied, and the mode of deposition of the polymer on the fibre examined. Fibre elasticity plays only a very small part in the non-felting mechanism, and it is concluded that resistance to milling shrinkage arises from the small reduction in scaliness coupled with local adhesion of both fibres and yarns. P. C.

Setting of Nylon Fabrics. G. K. Mecklenburgh. *J. Textile Inst.*, **41**, P 161–P 175 (April 1950).

Nylon fabrics may be set to prevent shrinkage on subsequent laundering by treatment with boiling water, pressure steam, and dry heat under various conditions. Under the more severe conditions, the fabrics are also set to shape and are resistant to creasing and distortion. Practical aspects of the setting processes are discussed. With dry heat setting, the time and temp. of treatment must be carefully selected to avoid yellowing and degradation due to thermal oxidation. W. K. R.

Mercerisation of Jute. R. R. Mukherjee and H. J. Woods. *Nature*, **165**, 818–819 (20th May 1950).

The complete transformation of crystalline native cellulose into the hydrate modification by the action of caustic soda is impossible in raw jute, and this is attributed to the partial reversibility of the native → soda cellulose reaction and not to the failure of caustic soda to penetrate the cellulose crystallites. The X-ray photograph of jute treated with 10% caustic soda indicates either a distortion of the soda-cellulose lattice or the co-existence of a range of transitional states between native cellulose and soda cellulose in jute. This has not been observed in other cellulosic fibres, and may be a consequence of extra-crystallite cellulose–lignin linkages. A. S. F.

Mechanism of Microbiological Decomposition of Cellulose. R. G. H. Siu. *Text. Research J.*, **20**, 281–288 (May 1950).

When fungi or bacteria fall on cotton fibres the outer non-cellulosic layer or cuticle is first digested, and then degradation of the cellulosic portions of the fibre itself occurs. Attack is highly localised and occurs more readily in the amorphous regions of the fibre. According to current views, the cellulose is first converted to cellobiose by the enzyme cellulase, and then the cellobiose is split into two molecules of glucose by the enzyme cellobiase. Some evidence suggests, however, that cellobiose is not a necessary intermediary in the chain of reactions, and that the organism is able to initiate attack on any glycosidic linkage along the chain. By topochemical methods it should be possible to introduce substituent groups along the chains so that the fibre is rendered not only mildew-proof but also water-repellent or light-resistant. P. C.

Anomalous Results of Mothproofing Tests. K. P. Lamb. *Nature*, **166**, 37 (1st July 1950).

Shrink-controlled woollen materials are mothproofed, during dyeing with an acid dye (Xylene Fast Blue), with (*a*) a substituted urea derivative, and (*b*) a sulphonic acid derivative of triphenylmethane. Mothproofing efficiency is determined before and after two, four, and six domestic-type washings. It is found that there is a progressive loss of proofing agent but a steady increase in efficiency of proofing. Tests carried out with agent (*a*), applied at 60°C. with no dye present, instead of 100°C., give the usual decrease of efficiency with decrease of agent. It is concluded that in the former case there is an apparent inhibition of initial proofing efficiency which is progressively removed by washing. J. W. B.

Catalytic Degradation and Oxidation of Cellulose. W. G. Parks, J. G. Erhardt, Jr., and D. R. Roberts. *Amer. Dyestuff Rep.*, **39**, P 294–P 300 (1st May 1950).

The effect of various flame-retardant agents on the catalytic decomposition of cellulosic materials has been investigated by studying the rate and mechanism of cellulose oxidation on the basis of the reaction products obtained under a variety of conditions. The vol. of carbon monoxide and carbon dioxide, and the amount and nature of tarry decomposition products, have been studied. Lithium and sodium carbonate and chloride and potassium chloride decreased tar formation. Afterglow was observed with all catalysts except borates, phosphates, cerium sulphate, and chromic, antimony, and zinc chlorides. In general phosphates have a marked effect on inflammability

and are most effective in reducing the amount of tar and carbon dioxide in the thermal decomposition of cellulose. A. S. F.

Thermal Behaviour of Fabrics at Flaming Temperatures. S. Coppick, J. M. Church, and R. W. Little. *Ind. Eng. Chem.*, **42**, 415–418 (March 1950).

The protective quality of a fabric may be defined as a function of the quantity and intensity of the heat supplied and generated, the area over which it is effective, and the coefficient of heat transfer. The combustion of cellulosic fabrics is discussed. Decomposition and oxidation proceed simultaneously. Flame-retardants reduce the quantity of inflammable tars in the decomposition products. The glowing action is caused by the oxidation of the solid decomposition products. Flame-retardants such as borax and metallic oxides have no inhibiting effect on afterglow and may enhance it, the best glow-retardants being the ammonium phosphates and, to a lesser extent, boric acid. In the presence of the effective glow-retardants, a large proportion of the carbon is oxidised to carbon monoxide, a reaction which is not sufficiently exothermic to be self-supporting; otherwise, most of the carbon is oxidised to carbon dioxide, a highly exothermic reaction. A cellulosic fabric treated with suitable flame- and glow-retardants maintains its structure, which acts as a thermal barrier and affords a good degree of protection by retarding the transfer of heat. It is shown that such a fabric has thermal protective properties equal to those of fabrics made from asbestos and glass fibre. W. K. R.

Evaluation of Flame-resistant Fabrics. J. M. Church, R. W. Little, and S. Coppick. *Ind. Eng. Chem.*, **42**, 418–427 (March 1950).

The acceptability of a flame-resistant fabric for a given purpose is dependent not only on its flame resistance, but also on other textile properties which may be altered by the treatment employed. Full details are given of standardised methods of determining flame resistance, rate of burning, and afterglow by the vertical, horizontal, and angle tests. Procedures are also described for testing the acceptability of the treated fabric by measuring the resistance to leaching by tap and sea water, perspiration, washing; the deterioration of the fabric or its flame-resistant properties on storage or exposure, and the effect of the treatment on fabric strength, porosity, and physiological properties, e.g. toxicity, skin abrasion, and heat load. Suggested schemes for preliminary and complete evaluation of a flame-retarding agent or treated fabric are outlined, and the results of the performance of typical treatments of the water-soluble, semi-durable, and durable types, when subjected to the tests described, are tabulated. W. K. R.

Statutory Requirements for Flame Resistance in Textiles. G. S. Buck, Jr. *Ind. Eng. Chem.*, **42**, 428–430 (March 1950).

Most textile flammability regulations which have been adopted in various parts of the U.S.A. relate to the flame-proofing of decorative materials in public buildings. An attempt has also been made to prevent the use of hazardous wearing apparel. The problems of defining a hazardous degree of flammability and of measuring the difference between dangerous and safe fabrics are discussed. The poor interlaboratory reproducibility of the present flammability tests indicates the need for improved methods before legislation of this type can be enforced. W. K. R.

Fire-retardant Textiles from a Consumer Standpoint. K. H. Barnard. *Ind. Eng. Chem.*, **42**, 430–432 (March 1950).

The requirements of a fire-retardant finish are discussed. It is considered that, to be acceptable to the consumer, a treated textile must not only be slow-burning, but must also retain, substantially unchanged, its original characteristics of strength, tearing resistance, drape, handle, comfort, colour, and durability. In addition the treatment must be cheap and must not cause dermatitis. W. K. R.

Commercial Application of Flame-resistant Finishes. R. W. Little, J. M. Church, and S. Coppick. *Ind. Eng. Chem.*, **42**, 432–440 (March 1950).

The methods commercially available for applying temporary and durable flame-resistant finishes to cellulosic textiles are reviewed; and bulk processing procedures are described in detail. W. K. R.

Durably Flame-retarding Cellulosic Materials. H. C. Gulledge, and G. R. Seidel. *Ind. Eng. Chem.*, **42**, 440–444 (March 1950).

A new durable flame-retardant finish for cellulosic fabrics known as Erifon (DuP) is described. The process consists essentially in impregnating the fabric with an aqueous solution of titanyl chloride and antimony trichloride in the presence of excess HCl for 1–15 min., and then neutralising with soda ash solution, rinsing, and scouring. Equipment required and problems of application are discussed. The finish withstands repeated mild laundering but not high-temp. alkaline laundering. Tensile strength and durability of the fabric are not impaired by the treatment, but the light fastness of some dyes is reduced. W. K. R.

Influence of Differently Coloured Light on Rate of Drying of Linseed Oil. E. Stock. *Seifensieder-Ztg.*, **73**, 233–238 (1947): *Chem. Abs.*, **44**, 4692 (25th May 1950).

A series of curves shows the changes in weight of linseed oil films exposed to light filtered through coloured glasses at room temperature in presence of various combinations of Soligen Pb, Mn, and Co. With Pb, Mn, or Co or small amounts of Pb–Mn or Co–Mn light of short wavelength markedly promotes drying. The effect generally decreases as the incident light passes from violet to brown and red; the latter, in fact, decelerates drying. With sunlight as the source the action was weaker than with diffused light. The decelerating effect of brown–red light was also weaker, and in presence of Pb–Mn (not of Co–Mn) could be eliminated. With Pb–Mn–Co, variations in the wavelength of the incident light had no effect; the films dried in the same time under red, blue, and violet light with both diffused light and sunlight. C. O. C.

PATENTS

Setting the Twist in Yarns. R. C. Allison and Alexander Smith & Sons Carpet Co. *U.S.P.* 2,499,444.

Highly twisted carpet yarns are given improved mechanical properties and rendered fast to aqueous treatments by treating them with saturated steam while they contain at least 30% by weight of moisture and then treating with an aldehyde. Carpets containing such yarn can be repeatedly wet-shampooed without the pile losing its twist. C. O. C.

Stabilising Fabrics containing Rayon. A. S. Stevenson, L. Beer, and Alrose Chemical Co. *U.S.P.* 2,497,519.

The fabric is treated in open width with a 30–50% aqueous solution of caustic alkali at 20–60°c. for a few seconds so as to saturate it rapidly. It is then squeezed to give a liquor retention of 60–100% on its dry weight and then, within 1 min. of the start of the caustic impregnation, neutralised directly without any prior rinsing, washed, dried, and adjusted to width. The whole process is conducted with no tension along the warp. C. O. C.

Stabilising Fabrics containing Cellulosic Rayon. Alrose Chemical Co. *B.P.* 637,656.

Fabric is treated continuously in open width while under no warpway tension by immersing it in a 30–50% solution of caustic alkali at 20–60°c. for not $>$ 10 sec., squeezing so that the fabric retains 60–100% of its weight of the liquor, neutralising directly without prior dilution of the alkali in the fabric, washing, drying, and adjusting to the predetermined width. C. O. C.

Crease-resisting. Linen Industry Research Assocn., D. A. Derrett-Smith, and R. W. Kinkead. *B.P.* 638,593.

Modification of *B.P.* 618,184 (J.S.D.C., **65**, 424 (Aug. 1949)). Materials containing bast fibres are thoroughly swollen and shrunk before being dried and then impregnated with the resin precondensate. They may be stretched between shrinking and impregnation, but not to the extent needed to bring them back to their original dimensions. The impregnated material is then baked and, if desired, soured and/or mercerised. C. O. C.

Fabrics from Twistless Alkali-resistant Yarn. B. P. Ridge and I.C.I. Ltd. *B.P.* 638,338.

Fabrics containing alkali-resistant yarn and highly polymerised polymethylene terephthalate yarn (the polymethylene group of which contains 2–10 C) are treated with aqueous caustic soda to remove some or all of the terephthalate yarn. C. O. C.

Oxidised Cellulose Gauze. W. O. Kenyon, C. C. Unruh, W. F. Fowler, Jr., and Eastman Kodak Co. *U.S.P.* 2,496,797.

Cellulose gauze is wound on a perforated drum, treated in a closed chamber with NO_2 vapour, then washed with cation-free water, and finally dried on the drum. C. O. C.

Adhesion of Rubber to Fibrous Materials. F. S. Perkerson and Callaway Mills Co. *U.S.P.* 2,499,774.

Better adhesion between cotton or rayon and rubber is obtained by treating the fibres with a mercapto compound, non-volatile at vulcanising temperature, which contains a polar group, e.g. thiosalicylic acid, before applying a rubber composition and vulcanising. C. O. C.

Improving the Fastness to Light of Bleached Jute. Indian Jute Mills Assocn. Research Institute and H. J. Callow. *B.P.* 639,449.

The fastness to light of bleached jute is improved by acetylating with acetic anhydride below its b.p. in presence of an alkali-metal acetate; e.g. the bleached jute is impregnated with potassium acetate to 100% imbibition, dried at 50°C., and heated for 5 min. in acetic anhydride at 100°C. J. W. B.

Reducing the Felting Power of Wool and Animal Hair. Stevensons (Dyers) Ltd., J. L. Raynes, and F. M. Stevenson. *B.P.* 638,580.

Modification of *B.P.* 569,730 (J.S.D.C., **61**, 302 (1945)). Wool, if desired in presence of other fibres, is treated with a dilute aqueous solution of a permanganate at not $> 60°C.$ and pH 5–10 before or after treating with a 0·5–10·0% aqueous solution of a sulphur-containing reducing agent, e.g. a bisulphite or a hydrosulphite, at pH 5·0–10·5. C. O. C.

Reducing the Felting Power of Wool. H. F. Clapham, A. L. Smith, and Harris Research Laboratories. *U.S.P.* 2,499,987.

Wool or material containing wool is treated at not $>$ room temperature and for a few seconds only and under such conditions that no reaction occurs with a hypohalite solution containing 1–6·75% available halogen. The temperature is then abruptly raised to not $< 125°F.$, e.g. by steaming the impregnated material. The reaction between the wool and the halogen takes place in a few seconds and very evenly. By this means chlorination of wool can be carried out as a continuous process. C. O. C.

Permanent Finish for Protein-containing Textiles. E. L. Kropa, A. S. Nyquist, and American Cyanamid Co. *U.S.P.* 2,499,653.

Protein-containing textiles, e.g. wool, treated with the copolymer of 2–20% of maleic anhydride and 98–80% of a lower alkyl acrylate containing 1–4 C, e.g. ethyl acrylate, have excellent shrinkage resistance, increased tensile strength, soft handle, and a permanent finish resistant to laundering. C. O. C.

Finishing Wool and other Animal Hairs with Formaldehyde–Resorcinol Condensates. N.V. Onderzoekingsinstituut "Research". *B.P.* 639,155.

Wool or other animal hairs are treated with an aqueous solution of a formaldehyde–resorcinol precondensate at pH 2·8–5·0 and then cured at 100–140°C. This renders the fibres more resistant to acids and alkalis, less liable to lose strength during bleaching, and more resistant to wear, and yields dimensionally more stable yarns and fabrics. C. O. C.

Decatising. W. N. Hadley and Parks & Woolson Machine Co. *U.S.P.* 2,498,416.

The fabric is wound on a foraminous cylinder and held firmly on it by a foraminous and flexible sheet of tough and non-stretchable material, e.g. rustless metal or plastic. Hot water or steam can then be passed radially through the wound fabric. This enables much more fabric to be treated at one operation, uses less heat, and produces a smoother and superior finish. C. O. C.

Papermakers' Felts. Orr Felt & Blanket Co. *B.P.* 638,275.

Papermakers' felts, which have been impregnated with a mixture of aqueous rubber latex and urea–formaldehyde condensate and then heat-cured, have high wettability, the same tensile strength dry and wet, high resistance to abrasion, and good dimensional stability. C. O. C.

Felting and Shrinking of Hat Bodies. M. T. Hoffman, Merrimac Hat Corpn., and Neumann-Endler Inc. *U.S.P.* 2,496,873.

When using a multiroller, the length of the oscillating motion working on the bat, the pressure, and the temperature of the water are progressively increased while the frequency of the oscillation is progressively reduced. This maintains optimum felting conditions throughout the whole operation. C. O. C.

Steam-spotting. W. M. Cissell. *B.P.* 638,641.

Steam-spotting of stained materials is effected by a spotting-gun which by suitable manipulation of the mixing-chamber valves ejects steam of any desired wetness or dryness, according to the nature of the fabric being cleaned. J. W. B.

Fixing Insoluble Substances on Fibres. British Rubber Producers' Research Assocn. and C. M. Blow. (III, p. 488.)

Review of Research and Development in the Field of Textiles during 1949. Textile Research Institute and Textile Foundation. (VI, p. 494.)

Stabilisation of Zein Filaments—Curing with Formaldehyde in Acidic Non-aqueous Media. C. B. Croston. (VI, p. 495.)

Loss of Weight in Kier-boiling, Width Contraction in Bleaching, and Length Increase in Finishing–Calendering Processes. N. H. Shah. (VII, p. 496.)

Elimination of Moisture from the Surface of Sheet Material prior to Metal Deposition. P. Alexander. (XI, p. 502.)

Light Stiffening of Rubber. R. G. Newton and W. C. Wake. (XIII, p. 502.)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

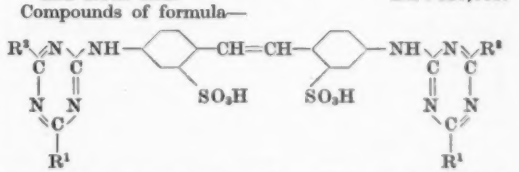
Reddening of Sulphite Pulp. II—Chemical Nature of the Reddening Component. E. Adler and S. Häggroth. *Svensk Papperstidning*, **53**, 321–326 (30th June 1950).

In experiments on the chemical nature of the substances or groupings responsible for the reddening of unbleached sulphite pulp, it was found that oxidised purified lignosulphonic acid gave a light transmission curve of the same general type as the light reflection curve of the reddened pulp. An apparently satisfactory model substance for the phenomenon of reddening was found in 3:3′-dimethoxy-4:4′-dihydroxystilbene, which oxidised under reddening conditions to the corresponding quinone, which gives to pulp a red colour of the same spectral type as the reddened pulp. S. V. S.

PATENTS

Whitening Agents for Paper. H. G. Cook, V. G. Morgan, and I.C.I. Ltd. *B.P.* 637,769.

Compounds of formula—



(R^1 = Cl or *p*-acetylaminoanilino; R^2 = hydroxyethylamino or bishydroxyethylamino) are exceptionally powerful whitening agents and do not cause yellowing of alum-sized paper. C. O. C.

Paper-coating Composition containing an Elastomeric Adhesive. S. D. Warren Co., J. C. Stinchfield, and F. Kaulakis. *B.P.* 637,583.

A pigment is dispersed in a primary aqueous dispersion of a synthetic rubberlike polymeric material acting as the essential adhesive, e.g. a copolymer of styrene and isoprene, an acrylate polymer with a plasticiser, or a copolymer of acrylonitrile and e.g. butadiene. Elasticity of the polymer may be induced by plasticising and a pigment : adhesive ratio of 2·5–4 : 1 may be employed. A mineral-coated paper is produced by coating the sheet or web with the composition, smoothing, and then calendering. S. V. S.

Paper-coating Composition. H. C. N. Heckel and Champion Paper & Fibre Co. *U.S.P.* 2,498,207.

Alkaline aqueous dispersions containing mineral pigment and oxidised cellulose have good bonding property for paper, are free-flowing even when they contain a high proportion of solids, and have good spreading properties. C. O. C.

Insecticidal Wallpaper. United Wallpaper Inc. *B.P.* 638,499.

Wallpaper coated with DDT and a protein binder, either as the ground coating for the decorative side or as the adhesive for prepasted paper, has good insecticidal properties. C. O. C.

Elimination of Moisture from the Surface of Sheet Material prior to Metal Deposition. P. Alexander. *B.P.* 639,099.

A roll of moisture-absorbent material, e.g. paper, is unwound and progressively exposed in web form in a vacuum chamber (0·05–0·5 mm. of mercury) to radiant heat, and re-rolled hot in a separate chamber at higher pressure. Plasticiser, e.g. glycerol, may be similarly removed from plastics, e.g. Cellophane. The treated material is ready for deposition of metal films by thermal evaporation *in vacuo*. J. W. B.

Diazotype Papers containing Alginate Sizing. General Aniline & Film Corpn. and S. C. Slifkin. *B.P.* 638,908.

Paper sized with an alginate size when converted into diazotype paper gives better penetration of the diazotype layers with less voids and deep spots. The dye images formed on it are of markedly increased visual density. C. O. C.

Cellulose Esters. British Celanese Ltd. *B.P.* 638,316.

When preparing organic cellulose esters, using sulphuric acid as catalyst, the cellulose ester is heated with an aqueous liquid of alkalinity < 5 p.p.m. (as $CaCO_3$) and with a surface-active agent, e.g. polyoxyethylene sorbitan monolaurate, to > 100°c. under pressure. The products have great stability. J. W. B.

Coating and Dyeing Cellulose Acetate Film. D. J. Evans and Dufay-Chromex Ltd. *B.P.* 638,979.

Cellulose acetate film 0·003–0·030 in. thick is evenly coated and dyed without streaks or ripple marks by using a dye dissolved in a low-b.p. organic solvent, the dye solution being brought to viscosity 4 centipoises by addition of cellulose acetate dissolved in an organic solvent of b.p. > 100°c. C. O. C.

Polymeric Sulphurous Esters— Stabilisers for Thermoplastic Cellulose Derivative Compositions. W. J. Myles, J. H. Prichard, and Celanese Corpn. of America. *U.S.P.* 2,497,135.

Compounds of formula HO·R·O·[SO·O·R·O]$_n$·SO·O·R·OH (n = 1–15; R = sat. straight hydrocarbon chain of 4–10 C and is the bivalent residue normally linking the OH groups of a polyhydric alcohol), e.g. polybutanediol sulphite, stabilise cellulose derivatives to coloration on exposure to light or heat. C. O. C.

Plasticisers for Cellulose Derivatives and Vinyl Chloride Polymers. W. H. Woodstock and Victor Chemical Works. *U.S.P.* 2,497,920.

Compounds of formula $(R^1{\cdot}O)_2PO{\cdot}CH{:}CR^2R^3$ (R^1 = Alk of 4–8 C, R^2 = H or Alk, R^3 = Alk or Ar, the total number of C atoms in the compound being 14–24) are excellent plasticisers for cellulose derivatives (except that the octyl esters are not compatible with cellulose acetate) and for vinyl chloride polymers or copolymers. C. O. C.

Insolubilised Cellulose Ethers useful as Textile Finishes or for Casting. A. L. Houk, L. H. Bock, and Röhm & Haas Co. (III, p. 488.)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

PATENTS

Fat Liquoring and Alum Tanning. B. Schiller, R. M. Beach, and Nopco Chemical Co. *U.S.P.* 2,496,640.

The skins are alum-tanned and then treated in the tanning liquor with a composition consisting of a leather-treating oil and a derivative alkylated with a dialkyl sulphate containing 2–4 C of a compound of formula $R^1{\cdot}CO{\cdot}[NH{\cdot}CH_2{\cdot}CH_2]_n{\cdot}NH{\cdot}R^2$ (R^1 = aliphatic chain of > 6 C, R^2 = hydroxyalkyl of 1–3 C, n = 1–3), and finally the pH of the solution is raised to precipitate the alum. *U.S.P.* 2,496,641.

Compounds of formula $R^1{\cdot}CO{\cdot}[NH{\cdot}CH_2{\cdot}CH_2]_n{\cdot}NH_2$ (R^1 = an aliphatic chain of > 6 C, n = 2–4) are used instead of those of the formula given in the preceding patent. C. O. C.

Chrome Tanning Baths. F. W. Binns, H. B. Channon, and Virginia Smelting Co. *U.S.P.* 2,500,020.

A chrome tanning bath prepared from two separately reduced solutions of alkali-metal dichromate is especially effective not only for use in a combination tannage, but for the improved quality of the tanned leather. C. O. C.

XIII— RUBBER; RESINS; PLASTICS

Light Stiffening of Rubber. R. G. Newton and W. C. Wake. *J. Rubber Research*, **19**, 9–27 (1950): *Chem. Abs.*, **44**, 4275 (10th May 1950), 5134 (10th June 1950).

Light stiffening is the increase in bending modulus of thin sheets of rubber or single-texture proofing when exposed to air and light. The effect decreases from surface to interior. Light stiffening is followed by formation of a resinous surface film, which involves contraction of the surface and hence surface crazing when the material is sufficiently rigid to resist the resulting tendency to curl. Experiments on the light stiffening of thin proofing and rubber films are described, and a simple method for measuring the increase in bending modulus is described with illustrations. This technique was used to study the influence of compounding ingredients and the wavelength of the radiation. The phenomenon is ascribed to oxidation activated by light, proof of which was obtained by experiments with films of rubber cut with a microtome and exposed to oxygen, nitrogen, and air. Attempts to obtain comparable results by use of seven different artificial lights were unsuccessful. Comparative tests of proofings vulcanised hot and vulcanised cold and of Neoprene and butyl rubber showed that light stiffening is characteristic of the polymer and is influenced only slightly by the mode of vulcanising. Influence of wavelength was studied chiefly with GR-S proofing. Wavelengths $> 540\,m\mu$. have insignificant effect on stiffening. The greater the energy passed by the filter (a technique using Wratten filters is described) the more rapid the rate of stiffening. Very little stiffening was caused by green or blue light; the effect of ultra-violet radiation increased with decrease in wavelength. Data are given on stiffening outdoors as a function of the season. Generally the greater the quantity of light energy the greater the stiffening, but there was an additional heat effect in summer. It is shown that the concurrent action of light and oxygen is the cause of stiffening, and that heat accelerates its rate. The mechanism of stiffening is discussed on the basis of theories developed by previous workers. The cantilever modulus test is shown to be far more sensitive, detecting changes long before the conventional scratch and folding tests do. A satisfactory artificial ageing test is to expose a very light-weight proofing to sunlight in spring or summer and measure the stiffening by the modulus test. This will show considerable stiffening in one week. The only effective way to prevent deterioration is to use compounds which interfere with the propagation of the chain reactions. These agents are antioxidants and deactivators, particularly when used jointly. Waxes are ineffective. Loading with carbon black confines the light-activated oxidation to a smaller depth and reduces stiffening. Absorbents of ultra-violet radiation, e.g. esters, which bloom to the surface, have some protective effect. In general, the more the protection from ultra-violet radiation, the longer the service life of proofing. Packing in dyed wrappers is advisable for products exposed or stored before service. C. O. C.

Polyurethans. VI— New Highly Elastic Synthetics, Vulcollans. O. Bayer, E. Müller, S. Petersen, H. F. Piepenbrink, and E. Windemuth. *Angew. Chem.*, **62**, 57–66 (1950): *Chem. Abs.*, **44**, 4709 (25th May 1950).

A detailed account of the polymers obtained in presence of a little water, by treating linear polyesters from aliphatic dicarboxylic acids and glycols with excess of certain di*iso*cyanates having hindrance structure. There are 65 references. C. O. C.

PATENTS

Aqueous Dispersions of Reaction Products of High Molecular Weight from Dihalogenohydrocarbons and Polysulphides. N.V. De Bataafsche Petroleum Maatschappij. *B.P.* 637,528.

Condensation in aqueous medium, in presence of water-soluble salts of sulphonic esters derived from alkenes or alcohols containing > 9 C, of dihalogeno derivatives of C_nH_{2n+2} hydrocarbons with alkali, alkaline-earth, or ammonium polysulphides yields finely dispersed latex-like products of good film-forming and adhesive power and stability. They may be used *inter alia* for impregnating paper and textiles, as leather or rubber substitutes, etc. C. O. C.

Resinous Coating Composition. Wingfoot Corpn. *B.P.*637,733.

Butadiene–styrene copolymers containing not < 80% of styrene produce coating compositions which yield films of excellent resistance to abrasion, toughness, and hardness without brittleness and which have a strong bond with the coated surface. Such coating compositions are readily produced by polymerising the dispersion of the monomers in presence of a thiol modifier containing 6–12 C. C. O. C.

Polymerisation of Substituted Ethylenes containing Organic Colouring Matter in presence of Azo Compounds. R. E. Burk and Du Pont. *U.S.P.* 2,500,023.

A polymerisable substituted ethylene, e.g. methyl methacrylate, containing organic colouring matter, is polymerised in presence of, as a catalyst, a colourless, non-aromatic azo compound, e.g. $\alpha\alpha'$-azodi*iso*butyronitrile, and in absence of a peroxide catalyst. Such azo compounds have no effect during polymerisation on many organic colouring matters, and less effect than peroxide catalysts on all organic dyes or pigments so far tested. C. O. C.

Dioctyl Tetrachlorophthalates—Plasticisers for Vinyl Halide Resins. G. J. Bohrer and General Electric Co. *U.S.P.* 2,496,852.

Dioctyl tetrachlorophthalates are plasticisers for vinyl halide resins, to which they impart marked heat resistance. C. O. C.

Vinyl Chloride–Ethylene Copolymers soluble in Aromatic Hydrocarbon Solvents. M. M. Brubaker, J. R. Roland, M. D. Peterson, and Du Pont. *U.S.P.* 2,497,291.

Copolymers of 74–90% vinyl chloride and 26–10% ethylene give not < 20% solutions by weight in aromatic hydrocarbon solvents. C. O. C.

Adhesives for Bonding Resins. United States Rubber Co. *B.P.* 639,185.

A polymerisable composition which on heating forms an adhesive, for bonding together materials of plasticised polyvinyl halide-containing resins, comprises 14–5 parts by wt. of an unplasticised polymer of a monomer containing a vinyl or vinylidene group, e.g. 90% of vinyl chloride and 10% of vinyl acetate, dissolved in 86–95 parts of a monomeric or partly polymerised liquid containing a vinyl or vinylidene group, e.g. methyl methacrylate. J. W. B.

Opaque Polyamide Films. Munising Paper Co. *B.P.* 639,327.

Pigment-free white opaque films are prepared by evaporating the solvent from a film of solution consisting of self-polymerised ω-aminocaproic acid in an alcoholic solvent containing about 5–40% water, by drying at 25–70°c. according to the amount of water present. J. W. B.

Reaction Products of Dicyandiamide with an Amine–Formaldehyde Condensate. J. R. Dudley, J. A. Anthes, and American Cyanamid Co. *U.S.P.* 2,497,073.

Products useful in coating and impregnating compositions and as cationic modifiers for urea–formaldehyde resins, especially those used for improving the wet strength of paper, are obtained by treating 1–1·3 mol. of dicyandiamide with 1 mol. of a primary aromatic monoamine or a secondary monoamine having not < 1 univalent aryl radical attached to the amino N previously condensed with 0·3–1·3 mol. of formaldehyde. *U.S.P.* 2,497,074.

The above products are heated with a urea–formaldehyde resin. C. O. C.

Linear Polyesters of Quinol, Saturated Glycols, and Dicarboxylic Acids. J. R. Caldwell and Eastman Kodak Co. *U.S.P.* 2,496,933.

Products of m.p. 90–300°c. are obtained by heating quinol with a glycol and a dibasic acid in presence of acetic anhydride. Used in coatings they impart hardness and gloss as well as resistance to deformation by moderate temperatures. They are resistant to ultra-violet radiation. C. O. C.

Decorative Films and Sheets. Courtaulds Ltd. and C. Ford. *B.P.* 638,774.

A decorative sheet is formed by taking a solution of a transparent film-forming material (1 part by wt.) in a volatile solvent (5–15) and uniformly dispersing throughout an insol. pigment other than metal powder. The soln. is spread in an even layer, and by controlled evaporation of the solvent a wrinkled surface is produced, the crests being more heavily pigmented than the troughs owing to dye migration. J. W. B.

Patterned Sheets of Polymeric Resin. I.C.I. Ltd. and A. L. L. Tompsett. *B.P.* 639,199.

Sheets of polymeric resin are prepared by polymerising one or more unsaturated organic compounds which contain only one $CH_2{:}C<$ group. Polymerisation is carried out while the monomeric or partly polymerised material, or both, are in contact with one or more forming surfaces, one of which may be patterned and at least one of which is made from a different thermoplastic resin, which is solid at the process temperature and which does not affect and is not affected by the resin being moulded. J. W. B.

Daylight-fluorescent Sheeting. J. L. Switzer and R. C. Switzer. *U.S.P.* 2,498,593.

A dye which exhibits a subtractive colour and fluoresces in daylight is dissolved in a transparent thermoset resin. The particles of this resin are evenly dispersed in a sheet of a transparent thermoplastic resin. The maximum weight of dye per c.c. of resin in which it is dissolved varies from 0·025 g. for yellow–greens to 0·015 g. for reds. The weight of dye must not be > 0·0005 g. per sq. cm. of surface of the sheeting. C. O. C.

Silicones. H. W. Kohlschütter. (III, p. 487.)

Plasticisers for Polyamides. G. R. Sido and Monsanto Chemical Co. (VI, p. 496.)

Solvents for Polyacrylonitrile. R. Hill, R. G. A. New, S. M. Todd, and I.C.I. Ltd. (VI, p. 496.)

Elimination of Moisture from the Surface of Sheet Material prior to Metal Deposition. P. Alexander. (XI, p. 502.)

Plasticisers for Cellulose Derivatives and Vinyl Chloride Polymers. W. H. Woodstock and Victor Chemical Works. (XI, p. 502.)

XIV—ANALYSIS; TESTING; APPARATUS

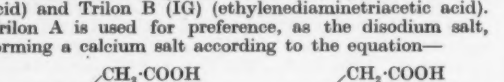
Constant-temperature Bath operating below Room Temperature. O. B. Darbishire. *Analyst*, **75**, 223–225 (April 1950).

A copper tank holding 4½ gal. of water is maintained at about 20°c. (extreme variation ± 0·3°c.) by allowing to pass into it a continuous and uniform stream of tap water (original temperature below 20°c.) which previously passes through an electrically heated tube; the overflow runs to waste. The electrical heater is controlled by a relay operated by a mercury–toluene thermoregulator or enclosed contact thermometer immersed in the bath. Thus cold and warm water are delivered alternately. The rate of water-flow is controlled by a constant-head device and adjusted by means of a screw-clip and rubber-tube connection, to allow for variation of tap-water temperature. Water-flow obviates the need for mechanical stirring to obtain the stated limits of temperature. H. I. S.

Assessment of Polymetaphosphates by means of "Schwarzenbach Complexes". J. Kubias. *Textil-Rund.*, **5**, 224–232 (June 1950).

Sodium hexametaphosphate (Calgon) is marketed in Czechoslovakia as Synthalgon (Synthesia) and in Switzerland as Alcopon (Uetikon). The estimation of polymetaphosphates by inorganic analysis is a long and complicated procedure, and has usually been carried out by finding the amount required to clarify a standard lime soap dispersion. The latter method is not too accurate, and an alternative

method is described, together with examples, using the "Schwarzenbach complexes", Trilon A (IG) (nitrilotriacetic acid) and Trilon B (IG) (ethylenediaminetriacetic acid). Trilon A is used for preference, as the disodium salt, forming a calcium salt according to the equation—



The product under test is dissolved in distilled water, and neutralised to phenolphthalein; excess $CaCl_2$ is added, followed by a soln. of the neutral disodium salt of nitrilotriacetic acid in slight stoichiometric excess, and the excess Ca^{2+} ions are titrated with 0·5 N-NaOH. The accuracy of the method is given as ± 5·6 mg. CaO per gram. B. K.

Novel Method of using Ion-exchange Resins. D. E. Weiss. *Nature*, **166**, 66 (8th July 1950).

A novel chromatographic method of using ion-exchange resins is described, whereby only one of two possible adsorption mechanisms associated with their use can function. Previous difficulties, associated with the inability of ion-exchange resins to fractionate mixtures containing aromatic molecules, have been resolved by adsorbing these on a dissociated ion-exchange resin the electrical charge of which has the same sign as the aromatic ions, so that only undissociated molecules can be adsorbed. Any change in pH which dissociates the adsorbed aromatic molecules will result in their desorption; e.g. acid dyes such as Methyl Orange, Fast Red A (*C.I.* 176), and Chicago Blue (*C.I.* 518) are adsorbed by Amberlite IRC–50 in its undissociated state in acid solutions, whereas no adsorption occurs in alkaline regions, where the resin and dyes are fully ionised. Similarly, the basic dye Methylene Blue is adsorbed by the polyamine resin Amberlite IR-4B under alkaline conditions, where the resin is unionised. H. H. H.

Detection of Indigosol Dyes. J. Lanczer. *Melliand Textilber.*, **31**, 360–361 (May 1950).

Two tests serve to distinguish between vat and Indigosol dyeings. Pieces of mercerised cotton are wrapped in the dyed material. A composite sample is treated in the first test with a solution of caustic soda and sodium hydrosulphite at 65°C., and in the second test is boiled with a solution containing 4 ml. caustic soda (38° Bé.), 4 g. hydrosulphite, and 4 ml. pyridine per 100 ml. Both vat and Indigosol dyes mark off in the second test, but only vat dyes as such in the first test. F. A.

Phase-contrast Microscopy. H. Reumuth. *Kolloid-Z.*, **115**, 44–53 (Oct.–Dec. 1949).

A full description is given of the important developments since 1945 in colloid, textile, and biological applications of this branch of microscopy. The procedure itself and typical examples with 10 illustrative diagrams are discussed in detail. H. H. H.

Estimation of the Residual Wool Fat on Tops combed in Oil. E. W. Clark and W. L. Thomas. *J. Textile Inst.*, **41**, T 236–T 240 (June 1950).

A method is outlined for the estimation of residual wool fat in wool tops oiled with Control Class A Oil (arachis), Modified Control Class A Oil (arachis containing 5% oleic acid), and Class A (1949) Combing Oil (specially processed sperm oil blended with castor oil). Residual oil and fat are extracted with anhydrous diethyl ether, and the refractive index is measured. Reference to a calibration curve for known mixtures of wool fat and combing oils enables the percentage of wool fat to be quickly and accurately obtained. The method can be applied only to tops not more than 3 weeks old, while prior to the top stage residual wool fat is liable to be non-uniform in refractive index. J. W. B.

Simple Method for Measurement of Hydrophilic Character of a Fabric. J. Chabert and Mme. Haberthur. *Bull. Inst. textile France*, No. 8, 51–54 (1948): *Chem. Abs.*, **44**, 5596 (25th June 1950).

The low end of a strip of the fabric mounted on a glass frame dips into an aqueous solution of 0·1 mg./litre sodium acridonesulphonate, and the time t taken for the solution to rise to a definite height up the strip is observed in ultraviolet radiation (in which sodium acridonesulphonate fluoresces). Absorbency is graded according to the parameter $1000/t$. C. O. C.

Spectrophotometric Determination of Small Amounts of Hydrogen Peroxide in Aqueous Solutions. T. C. J. Ovenston and W. T. Rees. *Analyst*, **75**, 204–208 (April 1950).

Microgram quantities of hydrogen peroxide in neutral aqueous solution are determined by liberating iodine from potassium iodide in the presence of ammonium molybdate catalyst, and measuring the optical absorption of the periodide I_3^- ion at 353 mμ. with a spectrophotometer or at 365 mμ. with a filter absorptiometer. The use of acid as catalyst causes photolysis of excess iodide and consequent erratic results. Large amounts of fluoride, chloride, and bromide do not interfere. The method is preferred to the starch–iodide method because of the variability of starch in composition and in colour after complexing, and to the titanium method because this is subject to interference by fluorides and other anions.

Procedure—Place not more than 4 ml. of suitably diluted sample (containing not more than 12 μg. of hydrogen peroxide) in a 10-ml. volumetric flask, add 5 ml. of 0·2 M. potassium iodide and 0·1 ml. of 0·5% (wt./vol.) ammonium molybdate solution, dilute to volume at 20°C., and after 5 min. in the dark measure the extinction in a 1-cm. cell at 353 mμ. (quartz spectrophotometer) or at 365 mμ. (photoelectric filter absorptiometer with mercury-arc source and suitable filters). Subtract the extinction reading for a reagent blank prepared similarly and at the same time with water in place of sample, correct for actual cell thickness, and read off the hydrogen peroxide content from a linear calibration graph prepared by operating similarly on known amounts of 0·0003% (wt./vol.) hydrogen peroxide. H. I. S.

Colour Systems and Atlases. C. L. Boltz. *Nature*, **166**, 129–132 (22nd July 1950).

Existing systems of colour specification and their atlases are reviewed, particular attention being given to the C.I.E., Munsell, and Ostwald colour systems. Lack of a corresponding colour atlas and the necessity for scientifically trained manipulators are considered the principal disadvantages of the first, while certain errors and inherent defects of the latter two are also criticised. The need for further standardisation is stressed. J. W. B.

Standardisation of Fastness Tests. Institut Textile de France. *Teintex*, **15**, 267–269 (June 1950).

Details are given of certain fastness tests which have been adopted as tentative standards by the Institut Textile de France. The tests are for fastness to dry cleaning, potting, sulphur stoving, brightening, and acid cross-dyeing. F. A.

Determination of the Fastness to Water Spotting of Dyeings and Prints. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A 2513. *Textil-Rund.*, **5**, 239 (June 1950).

A standard method is given for testing and assessing the fastness to water spotting of dyed and printed materials. B. K.

Determination of the Fastness to Acids of Dyeings and Prints. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A 2541. *Textil-Rund.*, **5**, 240 (June 1950).

Standard methods are given for testing and assessing the fastness to acids of dyed and printed textiles, using 50 g. sulphuric acid (sp. gr. 1·82) per litre and 300 g. acetic acid 100% per litre. B. K.

Determination of the Fastness to Alkali of Dyeings and Prints. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A 2546. *Textil-Rund.*, **5**, 241 (June 1950).

A standard method is given for testing and assessing the fastness of dyed and printed textiles to alkali, in which 10 g. soda ash per litre is used. B. K.

Flake Metal Powders—Application, Manufacture, and Testing. H. Meyersberg. (IV, p. 491.)

Method of Evaluating Protective Colloids for Vat Dyeing. P. Wengraf. (VIII, p. 497.)

Statutory Requirements for Flame Resistance in Textiles. G. S. Buck, Jr. (X, p. 500.)